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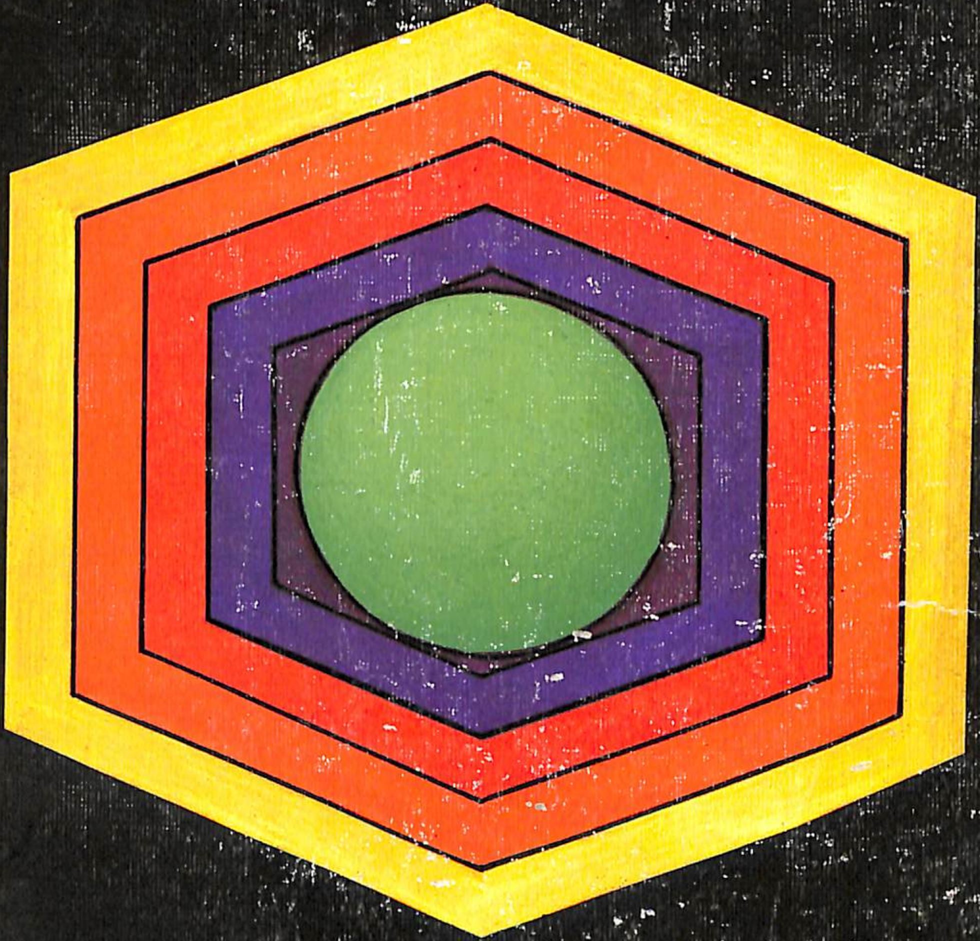
CHEMISTRY

TEXTBOOK FOR SCHOOLS

Yu. V. Khodakov, D. A. Epshtein, P. A. Gloriozov

PART TWO



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ХИМИЯ

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INORGANIC

CHEMISTRY

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Yu.V. Khodakov, D.A. Epshtein, P.A. Gloriozov

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Symbols

△	exercise
?	question
■	home assignment

1 Electrolytic Dissociation

Basing our investigations on the periodic law and the theory of atomic structure we have begun to study the chemical elements. For a better understanding of the material we shall now get acquainted with some new, very important conclusions that can be derived from the electron theory of atomic structure that explains the general properties of chemical compounds of each class (oxides, acids, bases, and salts).

1.1 Electrolytes and Nonelectrolytes

We have become acquainted with two types of chemical bonding, namely covalent (bonding between nonmetal atoms) and ionic (bonding between metals and nonmetals).

Molecules of ionic compounds can also exist in their vapours. Molecules of sodium chloride, for example, are formed in this way during the burning of sodium in chlorine. As molecules near one another they become mutually attracted by their oppositely-charged ions. The first step in the formation of an ionic crystal lattice from ionic molecules is shown in Fig. 1.1. The arrows that point at each other indicate the mutual attraction of oppositely-charged ions, while the arrows that point outside, show mutual repulsion of ions having the same charge.

We already know compounds of more complicated composition. These are hydroxides of metals and salts of oxyacids. What kind of chemical bonding accounts for their existence?

Bonds of both types are present in hydroxides and salts. Atoms of the elements composing a hydroxide ion or an acid residue are connected by covalent bonds while metals and hydroxide ions or metals and acid residues are held together by ionic bonds. Crystals of alkalis and salts of oxyacids are thus composed of ions, just like salts of binary acids (e. g. Na^+Cl^-). Metal ions bear a positive charge and the hydroxide ions, the ions of acid residues are charged negatively. It follows that not only charged atoms but charged groups of atoms can be ions. Formulas of bases and salts of oxyacids can therefore be given as

$$Na^+(OH)^-, \quad Ca^{2+}(OH)_2^-, \quad Na^+(NO_3)^-, \quad Al_2^{3+}(SO_4)_3^{2-}$$

One may expect that substances with ionic bonds will differ in their properties from substances with covalent bonds. This is confirmed by the study of electric conductivity of solutions of substances with covalent and

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Owing to the interaction between acid and water, the polar bond between hydrogen and acid residue becomes ionic and the acid molecules fall into ions. Nitric acid HNO_3, for example, falls into hydrogen ions H^+ and nitrate ions NO_3^-.

Decomposition of an electrolyte into ions during dissolution in water or during melting is called electrolytic dissociation.

When compounds with covalent nonpolar or low-polar bonds, e.g. sugar, are melted or dissolved in water, their crystals only fall into separate molecules and do not form ions. A solution or a melt of sugar does not therefore conduct electricity.

The theory that explains the special behaviour of electrolytes in the molten or dissolved state by their dissociation into ions is called the *theory of electrolytic dissociation*. The author of this theory is a Swedish scientist Svante August Arrhenius.

?

1. How can electric conductivity of electrolyte solutions be explained?
2. What substances fall into ions? Explain this from the standpoint of the theory of chemical bonds.

1.3

Mechanism of Electrolytic Dissociation

Why do electrolytes dissociate in water but not, for example, in kerosene? The hydrogen atoms are connected in water molecules with the oxygen atom by covalent polar bonds. The electron pairs connecting the atoms are displaced from the hydrogen atoms to the oxygen and the positive charge is therefore concentrated on the hydrogen atoms while the oxygen atom is charged negatively.

In order to examine the mechanism of electrolytic dissociation it is necessary to consider not only polarity of the bonds between the hydrogen and oxygen atoms in the water molecule but also polarity of the water molecule itself. The following can serve as a proof of the polarity of the water molecule.

The bonds of each hydrogen atom with that of oxygen in the water molecule are arranged at a certain angle and the centres of the positive and negative charges in the molecule do not therefore coincide at the same point. If only the mutual perpendicularity of the axes of the electron clouds formed by *p* electrons of the oxygen atom is taken into consideration, the angle between the bonds in question would be 90°. In fact this angle is 105° (Fig. 1.3). The deviation of the angle from the expected value is explained by mutual repulsion of the atoms bearing the same charge.

The polar molecule of water (a dipole) can be shown as an ellipse with indication of the charge on the poles by the plus and minus signs ("+" and "−").

When a salt crystal is placed in water (Fig. 1.4), the molecules of the latter are attracted to the ions on the surface of the crystal: by their negative poles

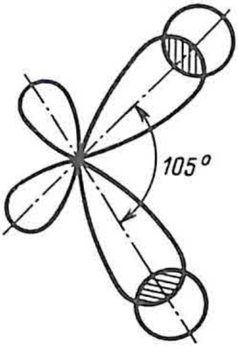


Fig. 1.3 Structure of water molecule. Clouds of unpaired electrons involved in the formation of chemical bonds are only shown

(oxygen atoms) they are attracted to the positive ions, and by their positive poles (hydrogen atoms) to the negative ions. A reaction of combination of the ions with the water molecules takes place. The reaction is known as *hydration of ions*, which is the main cause of dissociation of electrolytes.

The molecules of water attached to the ions significantly weaken the attraction of the ions to one another, and the bonds between the positive and negative ions in the crystal lattice break. The hydrated ions disjoin.

Consider another example using sodium chloride to illustrate the effect of ion hydration on the electrolytic dissociation.

In order to destroy the crystal lattice of sodium chloride taken in the quantity of one mole, 774 kJ are needed. If the energy of heat motion of water molecules were only used to break the lattice, the temperature of water taken at 20°C would drop so much that water would freeze. This does not happen and the temperature of water during dissolution of sodium chloride drops only slightly. Where is the energy required to dissociate the salt taken from? The question was only answered when it was established that dissociation is caused by a chemical process in which hydrated (solvated)

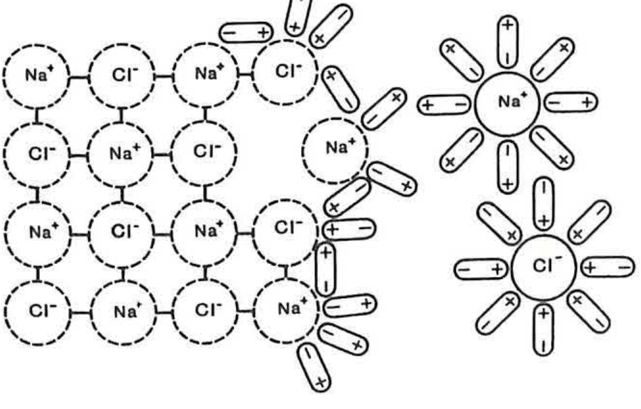


Fig. 1.4 Electrolytic dissociation of sodium chloride in an aqueous solution

ions are formed, the process that is accompanied by the liberation of large amounts of energy.

If the total energy of hydration of all ions present in the crystal is greater than the energy required to break down all bonds between them, the dissolution process is attended by the evolution of heat and the temperature of the solution rises. If this total energy is lower, the dissolution process is associated with absorption of heat.

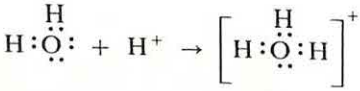
It can be understood now why electrolytic dissociation occurs in water but not in kerosene. No conditions for dissociation are provided in kerosene because the molecules of all substances (hydrocarbons) contained in kerosene are nonpolar.

Of course, the molecules of water that were attracted to the ions during dissolution of the crystal remain bonded with them in solution. The composition and properties of the ions contained in solution are therefore not the same as those of ions contained in the crystal lattice. We already know that anhydrous copper sulphate $CuSO_4$ is colourless. This means that the Cu^{2+} and SO_4^{2-} ions that make up the crystal lattice of the sulphate are colourless. When the Cu^{2+} ions combine with water molecules during dissolution they turn blue (the colour characteristic of copper salt solutions). This colour is therefore due to the hydrated ions of copper, i.e. ions connected with the water molecules.

If we carefully evaporate a copper(II) sulphate solution to the dry state, blue crystals of vitriol will remain in the dish instead of the white powder of copper(II) sulphate. The blue crystals contain hydrated ions of copper $(Cu \cdot 5H_2O)^{2+}$ and SO_4^{2-} ions. The formula of blue vitriol is $CuSO_4 \cdot 5H_2O$.

The water contained in the crystals is known as *water of crystallization*, while substances containing water of crystallization are called *crystal hydrates*. Many salts are actually crystal hydrates. Commonly used salts are crystal hydrates like iron vitriol (green copperas) $FeSO_4 \cdot 7H_2O$, gypsum $CaSO_4 \cdot 2H_2O$ and soda $Na_2CO_3 \cdot 10H_2O$.

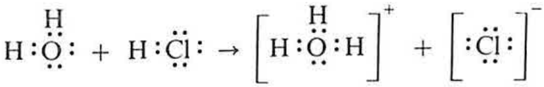
Like salts and alkalis, acids also fall into ions in water. Water molecules are attracted to the polar molecules of the acid, and displace to an even greater extent the electron pair from the hydrogen towards the acid residue. The bond between hydrogen and the acid residue becomes ionic and breaks down. A bond arises between the acid proton and the water molecule. The bond is formed by one of the two electron pairs in the outer electron layer of the oxygen atom:



$$\mathrm{H}:\overset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}}: + \mathrm{H}^+ \rightarrow \left[\mathrm{H}:\overset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}}:\mathrm{H}\right]^+$$

The *hydronium ion* is formed, in which there are three covalent bonds between hydrogen and oxygen. These three bonds were formed by different mechanisms: two were formed by pairing the electrons of the oxygen atom with the electrons of the hydrogen atoms, while the third was formed by attaching the proton to the free electron pair of the oxygen. In the latter case the oxygen atom of the water molecule gives off a pair of electrons (not one electron) to build the covalent bond with the proton. The oxygen atom is called the *donor* and the proton, the *acceptor*. The mechanism of formation of such covalent bonds is called *donor-acceptor*. But irrespective of the mechanism of formation, all three bonds in the hydronium ion are equivalent.

Electrolytic dissociation of hydrogen chloride in an aqueous solution can be shown as this:



$$\mathrm{H}:\overset{\mathrm{H}}{\underset{\cdot\cdot}{\ddot{\mathrm{O}}}}: + \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \rightarrow \left[\mathrm{H}:\overset{\mathrm{H}}{\underset{\cdot\cdot}{\ddot{\mathrm{O}}}}:\mathrm{H}\right]^{+} + \left[:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:\right]^{-}$$

All other ions (not only the hydrogen ions) are hydrated in solution, i.e. they are bonded with water molecules. But the water molecules that are attached to the ions are disregarded because they normally do not take part in chemical reactions between electrolytes.

?

1. What is electrolytic dissociation? What is the role of water in it?
2. How do the ions of the crystal lattice of sodium chloride and sodium hydroxide differ from the ions contained in solutions of these substances?
3. Can crystalline substances dissolve without absorption or liberation of heat? Explain your answer.
4. Explain the mechanism of electrolytic dissociation of hydrogen iodide during its dissolution in water.

1.4 Equations of Dissociation of Acids, Alkalis, and Salts

Like any other chemical reactions, dissociation of electrolytes can be expressed by equations. Acids dissociate into hydrogen ions and acid residue ions, e.g.

$$\begin{aligned} &HCl = H^+ + Cl^- && \text{or } HCl + H_2O = H_3O^+ + Cl^- \\ &HNO_3 = H^+ + NO_3^- && \text{or } \ldots\ ? \\ &H_2SO_4 = 2H^+ + SO_4^{2-} && \text{or } \ldots\ ? \end{aligned}$$

Consider one of the above examples, the electrolytic dissociation of sulphuric acid.

Unlike hydrogen atoms, hydrogen ions do not unite in pairs. They can neither pair nor approach each other because they are charged similarly, and similarly charged particles are known to repel one another.

The equation shows the dissociation of sulphuric acid as a single process but in fact dissociation takes place in stages and the ions of hydrogen are not eliminated from the acid molecule all at once but one after another:

$$H_2SO_4 = H^+ + HSO_4^-, \quad HSO_4^- = H^+ + SO_4^{2-}$$

Alkalis dissociate into metal ions and hydroxide ions, for example:

$$NaOH = Na^+ + OH^-$$
$$Ca(OH)_2 = Ca^{2+} + 2OH^-$$

Salts dissociate into metal ions and acid residue ions:

$$\begin{aligned} NaNO_3 &= Na^+ + NO_3^- \\ K_2CO_3 &= 2K^+ + CO_3^{2-} \\ Al_2(SO_4)_3 &= 2Al^{3+} + 3SO_4^{2-} \end{aligned}$$

Since molecules or crystals of substances are electrically neutral entities, the total charge of positive ions formed during dissociation is always equal to the total charge of negative ions.

? 1. What do the following equations describe: (a) $NaCl = Na^+ + Cl^-$, (b) $Na^+ + Cl^- = NaCl$? How does each process occur in the home?

△ 2. Write equations for electrolytic dissociation in solutions of the following substances: (a) hydriodic acid, (b) selenic acid H_2SeO_4, (c) lithium hydroxide, (d) barium hydroxide $Ba(OH)_2$, (e) copper(II) nitrate $Cu(NO_3)_2$, (f) iron(III) sulphate, (g) sodium sulphite, and (h) sodium hydrogen sulphate $NaHSO_4$ (its solution colours litmus red). Check to see if the total charges of positive and negative ions are equal. Read the first two equations.

3. Write equations for the three steps of dissociation of phosphoric acid H_3PO_4. Check to see if the total charges of positive and negative ions are equal.

1.5

Degree of Electrolytic Dissociation. Strong and Weak Electrolytes

We know that electrolytes in aqueous solutions dissociate into ions. A question naturally arises: do all molecules of the electrolyte dissociate into ions in solution, or do some molecules remain that do not break down?

First of all it is necessary to remember that electrolytic dissociation is a reversible chemical process: the electrolyte molecules fall into ions and these ions simultaneously recombine into the starting molecules in the same solution. For example, some molecules of acetic acid fall in an aqueous solution into hydrogen ions and acid residues, and at the same time the hydrogen ions and acid residues combine into molecules of acetic acid.

In order to emphasize (whenever necessary) this special property of electrolytic dissociation the sign of reversibility ⇄ is substituted in chemical equations for the sign of equality. The equation of dissociation of acetic acid is written as follows:

$$HR \rightleftarrows H^+ + R^-$$

where R is acetic acid residue.

The study of solutions has shown that depending on the chemical nature of the electrolyte and its concentration, its solution may contain many undissociated molecules and only a few ions; or it may contain only a few molecules of the electrolyte and many ions. A solution of an electrolyte may contain no molecules at all since they all may break down into ions.

The quantitative measure of dissociation of a given electrolyte in a given solution is defined as its *degree of dissociation.*

Degree of dissociation α is the ratio of the number of molecules that break down into ions to the total number of molecules of the electrolyte in solution:

$$\alpha = \frac{\text{number of dissociated molecules}}{\text{total number of electrolyte molecules}}$$

The dissociation degree is expressed either in fractions of unity – which vary from zero (dissociation is absent) to 1 (complete dissociation) – or in per cent.

If the degree of dissociation of an electrolyte in a solution is, for example, 1/4 this means that each fourth molecule of the electrolyte has broken down into ions, while three molecules remain undissociated.

How does the degree of dissociation of an electrolyte in solution change with its concentration?

The degree of dissociation of an electrolyte in solutions always increases with decreasing concentration of the electrolyte, i. e. the dissociation degree increases with dilution because the ions become separated to greater distances and their recombination into molecules becomes less probable.

Anhydrous acetic acid does not conduct electricity when tested by the known method, because it contains no ions. As water is gradually added, the lamp comes on and its light becomes more intense: the acid now contains ions and their concentration increases with the dilution of acetic acid.

Electrolytes, the dissociation degree of which is high even in relatively concentrated solutions (1 or 100%), are *strong electrolytes*, while electrolytes whose dissociation degree is low even in dilute solutions, are *weak electrolytes.* Thus, *strong electrolytes are substances that readily break down into ions and weak electrolytes are substances that break down into ions with difficulty.*

Table 1.1

The Dissociation Degree of Electrolytes in Solution with Concentration of 0.1 mol/litre at a Temperature of 18 °C

Electrolyte	Degree of dissociation, %	Electrolyte	Degree of dissociation, %
Nitric acid	about 100	Acetic acid	1.4
Hydrochloric acid	about 100	Hydrosulphuric acid	0.1
Sulphuric acid	about 100	Potassium hydroxide	about 100
Phosphoric acid	20	Sodium hydroxide	about 100
Sulphurous acid	20	Calcium hydroxide	about 100
Hydrofluoric acid	8		

The dissociation degree of acids and alkalis determines their strength. Whether an acid will be strong or weak, depends on the ratio of the energy, spent on eliminating protons from the acid molecules, to the energy evolved during attachment of the protons to the molecules of water. An acid is strong if the energy evolved during attachment of the proton to the water molecule is higher than the energy spent to eliminate the proton from the acid molecule. Of the acids that we already know, nitric HNO_3, sulphuric H_2SO_4, and hydrochloric HCl acids are strong acids. The hydroxides of the alkali metals (NaOH, KOH, etc), and hydroxides of barium $Ba(OH)_2$ and calcium $Ca(OH)_2$ are strong bases. With very rare exceptions (cupric chloride), salt solutions contain no undissociated molecules. Salts are strong electrolytes, no matter from what acids or bases (strong or weak) they are formed.

Very sensitive instruments detect an extraordinarily low conductivity of pure water. This means that water contains ions as well. Water dissociates insignificantly into the hydrogen ion and the hydroxide ion:

$$H_2O \rightleftarrows H^+ + OH^-(2H_2O \rightleftarrows H_3O^+ + OH^-)$$

Why is the second proton not eliminated from the water molecule to give an O^{2-} ion? The first proton is eliminated by overcoming the attractive force of a uninegative ion OH^- while the second proton would have overcome a much stronger attraction of a dinegative ion O^{2-}.

The dissociation degree of water is about 10^{-9} (at room temperature), i.e. only one molecule per milliard dissociates into ions. Water is so weak an electrolyte that its dissociation would be normally ignored.

? 1. What does the expression "The degree of dissociation of acetic acid in a given solution is 0.3" mean?
△ 2. A solution of a weak electrolyte is given. How can its dissociation degree be increased or decreased?
3. What are strong and weak electrolytes?
4. In molecules of what acids (strong or weak) are hydrogen atoms more strongly bonded to acid residues?
5*.[1] Why can water be regarded as both an acid and a base?
6*. What four types of ions are contained in an aqueous solution of sodium sulphate (e.g. with the concentration of 1 mol/litre)? Which of them are contained in the greatest and which in the smallest numbers?
7. Indicators are usually salts of weak organic acids in which molecules have one colour (e.g. methyl orange is red) while their negative ions have different colour (yellow in the case of methyl orange). Why does the colour of methyl orange change from orange to red when acid is added?

1.6

Properties of Electrolyte Solutions

Like many original ideas, the theory of electrolytic dissociation was first regarded with suspicion by contemporaries. Some simply rejected the idea that table salt, when it is added to soup, might break down into sodium and chloride ions, for everyone knew what sodium and chlorine looked like in the free state. Free sodium 'dissolves' in water to evolve hydrogen, while no hydrogen can be detected during the dissolution of table salt. Free chlorine is poison, whereas the right amount of salt added to various foods makes it taste better and is useful to the human body. But free sodium consists of electrically neutral sodium atoms Na while free chlorine is made up of chlorine molecules Cl_2. A solution of table salt does not contain atoms of sodium but its ions Na^+; nor does the solution contain chlorine molecules but it contains the chloride ions Cl^-.

---

[1] Answers to the problems marked with an asterisk are given at the end of the textbook.

The chemical activity of free sodium depends on the presence in its atoms of a valency electron which is given off by sodium during its reaction with water: hydrogen is liberated and the sodium atom converts into the Na^+ ion. Table salt contains sodium in the form of its ions Na^+, which pass from the crystal lattice into solution.

The chemical activity of free chlorine (its poisonous effect on the human body in particular) depends on the one missing electron which is required to complete its outer electron layer. The chloride ion contained in the crystals of table salt or its solution has gained the missing electron and its properties are therefore quite different from those of the free chlorine. Unlike chlorine molecules, the chloride ions are colourless, harmless, and have no odour. The solution of table salt containing the chloride ions and sodium ions is colourless, odourless, and harmless. The different properties of atoms and ions of one and the same element thus depend on their different structure.

Solutions of all acids have some common properties. Solutions of all alkalis, of all salts of a given metal, and of salts of a given acid also have some properties in common. How does the theory of electrolytic dissociation explain these facts?

It should be remembered that each type of hydrated ions has specific properties that show themselves in the properties of electrolyte solutions irrespective of the presence of other ions or molecules in it.

Acids dissociate into hydrogen ions and acid residue ions. Solutions of all acids thus contain one and the same type of ions, namely the hydrogen ion H^+. The sour taste of the H^+ ions (to be more accurate of the H_3O^+ ions) accounts for the specific taste of foods seasoned with vinegar (acetic acid solution). The common properties of acids are not the properties of acid molecules but of the hydrogen ions contained in them.

Alkalis dissociate into metal ions. and hydroxide ions. Solutions of all alkalis thus contain one and the same type of ions, namely the hydroxide ions OH^-. Just as the hydrogen ions account for the acid properties, so the alkaline properties depend on the presence of the hydroxide ions. The soapy feel of alkali solutions, their reaction to litmus, and destruction of vegetable and animal tissues, are the properties that depend not on their molecules but rather on the hydroxide ions contained in their solutions.

Hydrated ions Na^+, K^+, Cl^-, NO_3^-, and SO_4^{2-} are colourless. Solutions of NaCl, KCl, $NaNO_3$, KNO_3 and Na_2SO_4 are therefore also colourless. Coloured ions are known as well. Any soluble salt of copper (with colourless acid residue ions) gives the same light blue colour when dissolved in

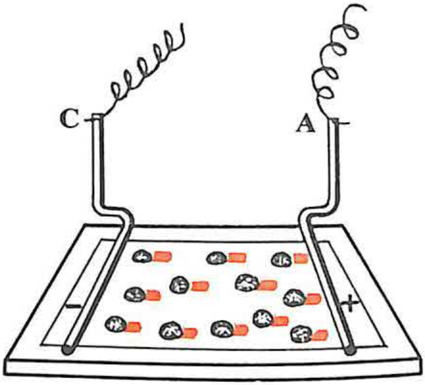


Fig. 1.5 Movement of ions in an electric field

a sufficient amount of water. The colour probably depends on the hydrated copper ion Cu^{2+}. Another example of a coloured negative ion is the acid residue ion of chromic acid H_2CrO_4. It is yellow. CrO_4^{2-} ions account for the yellow colour of solutions of the salts of chromic acid, e. g. K_2CrO_4.

Salts containing coloured ions can be used to prove the presence of an electric charge on the ions. Place a few grains of a coloured salt, e. g. $CuCl_2$ or K_2CrO_4, on a sheet of blotting paper wetted with some colourless electrolyte solution: the salt crystals will dissolve to form round coloured spots on the paper. But if before dropping the crystals on the paper we place two electrodes connected to the source of electricity as shown in Fig. 1.5, the picture will be different: coloured streaks will extend from each crystal, toward the negatively charged electrode if positively charged ions of the salt are coloured, and toward the positive electrode if the colour derives from negative ions.

Movement of ions toward the negative electrode (cathode) or toward the positive electrode (anode) is explained by attraction of the corresponding ions by the electrodes.

Positively charged ions attracted by the cathode are called cations and negatively charged ions attracted by the anode are called anions.

Strong electrolytes practically completely dissociate in aqueous solutions. The properties of aqueous solutions of strong electrolytes are therefore the properties of the ions contained in them. In addition to ions, solutions of weak electrolytes contain undissociated molecules. These are responsible for the specific properties of such solutions, i. e. of a given electrolyte. The odour of acetic acid solutions, for example, is due to the undissociated molecules contained in them.

?

△

1. Compare the properties of free iodine and the iodide ions.
2. How can the presence of hydrogen ions, hydroxide ions and ions of sulphuric acid residue be detected in solutions?
3. What properties do the hydrogen and hydroxide ions impart to electrolyte solutions?

4. The presence of what ions accounts for (a) the ability of hydrochloric acid and its soluble salts to form precipitates in reactions with silver nitrate, (b) the ability of sulphuric acid and its soluble salts to form precipitates with soluble salts of barium?

5. Potassium permanganate $KMnO_4$ is used as a disinfectant, to treat minor injuries. What accounts for the crimson colour of its solution?

6. How can the charge of the ions (positive or negative) be identified in a coloured solution?

7*. When electric current was applied to the electrodes of the apparatus shown in Fig. 1.5, red streaks moved from crystal of an unknown test substance to the anode, and green streaks to the cathode. What can we say about the test substance?

8. Which of the following ions are cations and which are anions: Cl^-, K^+, Ca^{2+}, OH^-, SO_4^{2-}? Are there coloured ions among them?

1.7

Ion Exchange Reactions

The chemical properties of strong electrolytes in solutions are due to the ions (either anions or cations) into which the electrolyte dissociates. But we have used molecular equations to describe exchange reactions between electrolytes in aqueous solutions, although electrolyte ions rather than molecules are involved in the reaction. In order to study the character of the reactions that occur actually, let us consider some reactions in which precipitates are formed.

When we pour together solutions of calcium chloride and silver nitrate, silver chloride AgCl precipitates while calcium nitrate remains in solution:

$$CaCl_2 + 2AgNO_3 = 2AgCl\downarrow + Ca(NO_3)_2$$

Both starting salts are strong electrolytes which are fully dissociated in an aqueous solution: $CaCl_2$ breaks down into Ca^{2+} and Cl^- ions, and $AgNO_3$ breaks down into Ag^+ and NO_3^- ions. One of the salts obtained by this reaction, $Ca(NO_3)_2$, remains in solution and dissociates into Ca^{2+} and NO_3^- ions. The equation of this reaction can therefore be written as

$$Ca^{2+} + 2Cl^- + 2Ag^+ + 2NO_3^- = 2AgCl\downarrow + Ca^{2+} + 2NO_3^-$$

This is a complete ionic equation.

What happens when we mix solutions? The ions Ag^+ and Cl^- only react to combine into silver chloride which precipitates. Meanwhile the ions Ca^{2+} and NO_3^- are not involved in the reaction and remain free, just as they were before the solutions were mixed. These ions can therefore be omitted in the equation:

$$2Ag^+ + 2Cl^- = 2AgCl\downarrow$$

The coefficients may be cancelled:

$$Ag^+ + Cl^- = AgCl\downarrow$$

This is the net ionic equation. It describes the essence of this and similar reactions. In accordance with this net ionic equation of the reaction between calcium chloride and silver nitrate solutions, the same precipitate may also be prepared by reacting any other solution containing the chloride ion Cl^- with any solution containing the Ag^+ ion. The general ability of hydrochloric acid and of all its soluble salts to form precipitates with silver salts that are insoluble in water or acids, is actually the property of the chloride ions Cl^-. We can thus formulate the following: the silver ion is the reagent for the chloride ion. In turn, the chloride ion is the reagent for the silver ion. If a cation can be used to identify an anion, the latter anion can in turn be used to detect the same cation.

If we mix together solutions of barium chloride and sodium sulphate, barium sulphate precipitates:

$$BaCl_2 + Na_2SO_4 = BaSO_4\downarrow + 2NaCl$$

The complete ionic equation of this reaction is:

$$Ba^{2+} + 2Cl^- + 2Na^+ + SO_4^{2-} = BaSO_4\downarrow + 2Na^+ + 2Cl^-$$

If we omit the symbols of the ions that are not involved in the reaction (Na^+ and Cl^-) the net ionic equation will be:

$$Ba^{2+} + SO_4^{2-} = BaSO_4\downarrow$$

The reaction between solutions of sodium sulphate and barium chloride thus consists in combination of the barium ions with the sulphate ions by which the insoluble barium sulphate is formed. The net ionic equation shows that barium sulphate precipitate may be prepared by mixing together any solution containing the Ba^{2+} ions with any solution containing the SO_4^{2-} ions, i.e. by reacting solutions of sulphuric acid or its salts with solutions of barium salts.

The general ability of sulphuric acid and all its soluble salts to form precipitate soluble neither in water nor in acids when added to barium salts is the property of the acid residue ions SO_4^{2-}. We can formulate: the barium ion is the reagent for the SO_4^{2-} ion, and vice versa.

Soluble but low-dissociating substances may also be formed by exchange reaction between electrolytes. Add sulphuric acid to a solution of any salt of acetic acid: the specific smell of acetic acid will be detected at once. Acetic acid is formed by combination of the H^+ ion (contained in the acid added) with the acid residue ions contained in the salt solution.

Let us designate the anion of acetic acid by R and describe the reaction by the following molecular equation

$$2NaR + H_2SO_4 = Na_2SO_4 + 2HR\uparrow$$

But both starting substances (NaR and H_2SO_4) and one of the reaction products (Na_2SO_4) are strong electrolytes: they fully dissociate into ions. Another reaction product is acetic acid. This is a weak electrolyte and molecules rather than ions prevail in its solution. We can now write the ionic equation of the reaction

$$2Na^+ + 2R^- + 2H^+ + SO_4^{2-} = 2Na^+ + SO_4^{2-} + 2HR\uparrow$$

Delete from the equation the formulas of the ions that are not involved in the reaction and cancel the coefficients, the net ionic equation will be

$$H^+ + R^- = HR$$

The essence of the reaction is thus the combination of the residue ions of acetic acid, contained in the solution of its salt, with the hydrogen ions contained in the sulphuric acid solution. Molecules of acetic acid are the reaction product.

All salts of acetic acid can thus be identified by a general sign – the odour of acetic acid that can be detected after addition of a strong acid.

When a solution of a strong acid, for example, sulphuric acid, is added to a solution of a salt of carbonic acid, for example sodium carbonate, an exchange reaction occurs. One might expect that the reaction products should be sodium sulphate and carbonic acid H_2CO_3. But carbonic acid is an unstable compound and it immediately decomposes into water and carbon dioxide. The solution 'boils' due to evolution of carbon dioxide bubbles. The molecular form of the equation is as follows

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2CO_3 \begin{array}{l} \nearrow CO_2\uparrow \\ \searrow H_2O \end{array}$$

Sodium carbonate, sulphuric acid, and sodium sulphate are strong electrolytes and they fully dissociate into ions in solution. The ionic equation of this reaction is thus:

$$2Na^+ + CO_3^{2-} + 2H^+ + SO_4^{2-} = 2Na^+ + SO_4^{2-} + CO_2\uparrow + H_2O$$

If we now omit the ions that were not involved in the reaction we have the net ionic equation

$$CO_3^{2-} + 2H^+ = CO_2\uparrow + H_2O$$

All salts of carbonic acid can be identified by vigorous bubbling ('boiling') after addition of a strong acid. The hydrogen ion is the reagent for the CO_3^{2-} ions.

Exchange reactions between electrolyte solutions occur if the reaction product is a low-dissociating substance or a substance that leaves the reaction system in the form of a precipitate or a gas. If low-dissociating, sparingly soluble, or gaseous products are not formed from the ions contained in solution, no reaction occurs after mixing electrolyte solutions.

If we mix together dilute solutions of sodium chloride and calcium nitrate, no reaction takes place because neither precipitate, gas nor low-dissociating substances are formed. If we write the molecular equation of the expected reaction

$$2NaCl + Ca(NO_3)_2 = 2NaNO_3 + CaCl_2$$

in the ionic form, we have

$$2Na^+ + 2Cl^- + Ca^{2+} + 2NO_3^- = 2Na^{2+} + 2NO_3^- + Ca^{2+} + 2Cl^-$$

The chemical composition of the solution has not changed.

All exchange reactions in solutions of electrolytes are associated with the combination of ions. Since molecules prevail in weak electrolyte solutions, we shall in future indicate ions of only strong electrolytes in ionic equations.

If we look attentively at equations of ion exchange reactions we shall find out that the oxidation numbers of the elements involved do not change. The exchange reactions thus differ substantially from oxidation-reduction reactions in which the oxidation numbers of the elements involved change.

One should not, however, understand that all reactions, in which the oxidation numbers of the elements do not change, are exchange reactions. Many addition and decomposition reactions also occur without alteration of the oxidation numbers of the elements involved.

?
△

1. Write complete and net ionic equations for reactions between: (a) potassium chloride and silver nitrate, (b) potassium hydroxide and copper(II) nitrate, (c) sodium sulphate and barium nitrate, (d) aluminium sulphate and barium chloride. Explain why the same net ionic equation describes the last two reactions.
2. Write complete and net ionic equations for reactions between solutions of: (a) nitric acid and calcium hydroxide, (b) barium hydroxide and sulphuric acid. Carry out the latter reaction in an apparatus used to test solutions for electrical conductivity (Fig. 1.2). Add the solutions one after another in small portions. How does the intensity of light of the electric bulb change?
3. Reactions between (a) crystalline sodium chloride and concentrated solution of sulphuric acid, (b) potassium hydroxide and nitric acid solutions, and (c) barium chloride and sodium sulphate solutions proceed to the end. Why?
4. Write equations of reactions between: (a) magnesium and oxygen, (b) potassium hydroxide and sulphuric acid solutions, (c) iron and copper(II) sulphate solution, (d) sodium oxide and water, and of decomposition (e) of water, and (f) of sulphurous acid. In which reactions do the elements change their oxidation numbers?

5*. Two moles of sodium nitrate and one mole of potassium sulphate are dissolved in 1 litre of water. What other two salts can be used to prepare the same solution?

1.8 Fundamentals of the Theory of Electrolytic Dissociation

From what we already know we can state the following:

1. Substances whose solutions conduct electric current are electrolytes. Soluble acids, bases, and salts are electrolytes.
2. Electrolytes in aqueous solutions, and also molten salts and alkalis, break down into ions from which the crystal lattice of alkalis and salts is composed; whereas acids dissociate into ions because the protons are eliminated from their molecules and combined with water molecules to give the hydronium ions H_3O^+.
3. The breakdown of electrolytes into ions is called electrolytic dissociation. Positively charged ions are called cations and negatively charged ions, anions.
4. Electrolytic dissociation is a reversible reaction and any solution of

weak electrolyte will usually contain ions and undissociated molecules at the same time.

5. The ratio of the number of undissociated molecules to the total number of electrolyte molecules is called the degree of dissociation of an electrolyte in a given solution. The dissociation degree increases with dilution of the electrolyte solution.

6. Some electrolytes almost fully dissociate even in relatively concentrated solutions. These are called strong electrolytes. Other electrolytes, whose dissociation degree is low, even in dilute solutions are weak electrolytes.

Svante Arrhenius was the first (1887) to explain the special behaviour of electrolytes in the molten or dissolved state by their dissociation into ions. Further scientific developments have contributed significantly to the improvement of the theory of electrolytic dissociation. Arrhenius believed that dissociation of electrolytes was a physical phenomenon, and he could not therefore explain the breakdown of electrolytes into ions in water. The Russian scientist I. Kablukov explained the cause of dissociation. Using the theory of the chemical nature of the dissolution process developed by Mendeleev, he treated electrolytic dissociation as a chemical interaction of electrolytes with water. The main cause of dissociation is hydration of ions. The energy liberated during this process is greater than that consumed during ionization of the solute.

1.9

Chemical Properties of Acids, Bases, and Salts According to the Theory of Electrolytic Dissociation

Acids. From the viewpoint of the theory of electrolytic dissociation, an acid is an electrolyte whose aqueous solution contains only positively charged ions of hydrogen and negatively charged ions of the acid residue.

1. *All acids, both soluble and insoluble, strong and weak, react with alkalis to form salt and water.*

As an example, let us consider the reaction of neutralization of a strong acid. Take a dilute solution of hydrochloric acid and add a dilute solution of sodium hydroxide until the resultant solution turns litmus paper violet. No precipitate is formed; nor does any gas evolve. But a reaction takes place and the solution no longer has a sour taste. If we now measure the temperature of the solution we can see that it has risen significantly: heat was liberated during the reaction. This is a neutralization reaction which we earlier expressed by the molecular equation

$$\mathrm{NaOH} + \mathrm{HCl} = \mathrm{NaCl} + \mathrm{H_2O} + Q$$

The starting substances (NaOH and HCl) and one reaction product (NaCl) are strong electrolytes: they fully dissociate into ions. The second reaction product is water, which as we know hardly breaks down into ions. The following complete ionic equation can now be written for the reaction of neutralization of hydrochloric acid by sodium hydroxide:

$$\mathrm{Na^+} + \mathrm{OH^-} + \mathrm{H^+} + \mathrm{Cl^-} = \mathrm{Na^+} + \mathrm{Cl^-} + \mathrm{H_2O}$$

If we now delete the ions that were not involved in the reaction we obtain the following net ionic equation

$$OH^- + H^+ = H_2O \quad \text{or } OH^- + H_3O^+ = 2H_2O$$

The same equation will be obtained if we replace hydrochloric acid by any other strong acid, and sodium hydroxide by any other alkali. Thus, *the reaction of neutralization of a strong acid by a solution of any alkali consists in the combination of the hydrogen ions* H^+ *with the hydroxide ions* OH^- *into undissociated molecules of water.*

This is confirmed by the fact that during neutralization of alkali solutions by strong acids one and the same amount of heat is liberated per each two moles of the formed water:

$$H_3O^+ + OH^- = 2H_2O + 55\ \text{kJ}$$

Salt does not usually precipitate during neutralization reactions because water interferes with combination of metal ions with acid residue ions that do not take part in the reaction. In order to isolate the salt the solution should be evaporated.

The same reaction takes place during the interaction between strong acids and bases that are practically insoluble in water, except that the hydroxide ions are eliminated from the alkali before it enters the reaction (during dissolution of the alkali in water), while the hydroxide ions of insoluble hydroxides are eliminated during the reaction proper. For example, if a solution of sulphuric acid is added to copper(II) hydroxide which is practically insoluble in water, the precipitate is dissolved and the solution turns blue, the colour being characteristic of the hydrated copper ions. The molecular equation for this reaction is

$$Cu(OH)_2 + H_2SO_4 = CuSO_4 + 2H_2O$$

Sulphuric acid is the strong electrolyte among the starting substances, and copper sulphate among the reaction products. The ionic equations for the reaction are therefore as follows:

$$Cu(OH)_2 + 2H^+ + SO_4^{2-} = Cu^{2+} + SO_4^{2-} + 2H_2O.$$

$$Cu(OH)_2 + 2H^+ = Cu^{2+} + 2H_2O$$

We can see now that substances do not always precipitate in ion exchange reactions. They can also be dissolved if the other reaction product is more difficult to dissociate into ions than the soluble precipitate. In our example water is such a product.

2. *In contrast to weak acids, strong acids react with basic oxides to form salts and water.* A reaction between cupric oxide CuO which is insoluble in water and sulphuric acid solution may be used by way of illustration. When the solution is heated, the precipitate dissolves and the solution turns blue (the colour characteristic of hydrated copper ions).

The molecular equation of the reaction is

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

The ionic equations are as follows

$$CuO + 2H^+ + SO_4^{2-} = Cu^{2+} + SO_4^{2-} + H_2O$$

$$CuO + 2H^+ = Cu^{2+} + H_2O$$

3. *Soluble acids enter exchange reactions with salts* but only if the salt formed in the reaction is insoluble, or if the acid formed is either insoluble, weak or unstable acid.

If hydrochloric acid is added to a solution of silver nitrate a white curd-like substance (silver chloride) precipitates

$$AgNO_3 + HCl = AgCl\downarrow + HNO_3$$

The ionic equations are:

$$Ag^+ + NO_3^- + H^+ + Cl^- = AgCl\downarrow + H^+ + NO_3^-$$

$$Ag^+ + Cl^- = AgCl\downarrow$$

If we add sulphuric acid solution to a solution of sodium silicate (the salt of insoluble silicic acid), a jelly-like substance precipitates

$$Na_2SiO_3 + H_2SO_4 = H_2SiO_3\downarrow + Na_2SO_4$$

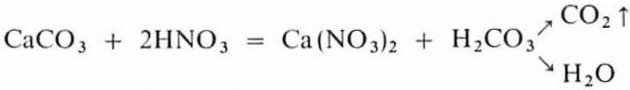
The ionic equations are

$$2Na^+ + SiO_3^{2-} + 2H^+ + SO_4^{2-} = H_2SiO_3\downarrow + 2Na^+ + SO_4^{2-}$$

$$2H^+ + SiO_3^{2-} = H_2SiO_3\downarrow$$

If sulphuric acid is added to a solution of a salt of the weak acetic acid, the solution will smell of acetic acid. The molecular equation and ionic equations for this reaction are given on page 22.

Take a piece of chalk (this is mainly calcium carbonate, the salt of an unstable carbonic acid) and place a drop of any acid on it: bubbles of carbon dioxide will evolve



$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2CO_3 \begin{array}{l} \nearrow CO_2\uparrow \\ \searrow H_2O \end{array}$$

The ionic equations for this reaction are

$$CaCO_3 + 2H^+ + 2NO_3^- = Ca^{2+} + 2NO_3^- + CO_2\uparrow + H_2O$$

$$CaCO_3 + 2H^+ = Ca^{2+} + CO_2\uparrow + H_2O$$

All the considered reactions of acids are exchange reactions. But acids can also enter reactions in which the oxidation numbers of the chemical elements can be altered.

4. *Acids soluble in water react with the metals that come before hydrogen in the electrochemical series* (see page 103) *to liberate hydrogen and form salts.* Zinc, for example, 'dissolves' in sulphuric acid to convert into zinc sulphate

with liberation of hydrogen from the acid

$$Zn^0 + H_2^+SO_4 \rightarrow Zn^{2+}SO_4 + H_2^0$$

$$\begin{array}{llll|l|l} Zn^0 & - & 2\bar{e} & \rightarrow Zn^{2+} & 2 & 1 \\ H^{1+} & + & 1\bar{e} & \rightarrow H^0 & 1 & 2 \end{array}$$

This reaction is called oxidation-reduction.

Bases. Some bases are soluble in water and others are practically insoluble. Soluble bases (alkalis) are electrolytes according to the theory of electrolytic dissociation. The aqueous solution of alkali contains only positively charged metal ions and negatively charged hydroxide ions.

1. *All bases (both soluble and insoluble) react with strong acids to form salts and water.*

Potassium hydroxide solution, for example, is neutralized by nitric acid solution

$$KOH + HNO_3 = KNO_3 + H_2O$$

The ionic equations of the reaction are

$$K^+ + OH^- + H^+ + NO_3^- = K^+ + NO_3^- + H_2O$$

$$H^+ + OH^- = H_2O \quad \text{or} \quad H_3O^+ + OH^- = 2H_2O$$

The insoluble base ferric hydroxide can be dissolved in hydrochloric acid. A yellow solution of ferric chloride is formed:

$$Fe(OH)_3 + 3HCl = FeCl_3 + 3H_2O$$

The ionic equations for this reaction are

$$Fe(OH)_3 + 3H^+ + 3Cl^- = Fe^{3+} + 3Cl^- + 3H_2O$$

$$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$$

This reaction occurs because water is more difficult to be split into ions than ferric hydroxide.

2. *Alkalis react with salt solutions to give new salts and new bases only when the expected new base or a new salt are insoluble in water* (consult solubility tables), for example:

$$CuSO_4 + 2NaOH = Cu(OH)_2\downarrow + Na_2SO_4$$

$$Cu^{2+} + SO_4^{2-} + 2Na^+ + 2OH^- = Cu(OH)_2\downarrow + 2Na^+ + SO_4^{2-}$$

$$Cu^{2+} + 2OH^- = Cu(OH)_2\downarrow$$

Amphoteric hydroxides. Amphoteric hydroxides are insoluble in water. Their acid and basic properties only show themselves in chemical reactions with alkalis and strong acids. They dissolve in them to eliminate the hydroxide ions (in acids) or the hydrogen ions (in alkalis).

Amphoteric hydroxides react with acids as insoluble bases, for example:

$$Zn(OH)_2 + 2HNO_3 = Zn(NO_3)_2 + 2H_2O$$

The ionic equations are:

$$Zn(OH)_2 + 2H^+ + 2NO_3^- = Zn^{2+} + 2NO_3^- + 2H_2O$$

$$Zn(OH)_2 + 2H^+ = Zn^{2+} + 2H_2O$$

Amphoteric hydroxides react with alkalis as insoluble acids, for example:

$$H_2ZnO_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

The ionic equations for this reaction are:

$$H_2ZnO_2 + 2Na^+ + 2OH^- = 2Na^+ + ZnO_2^{2-} + 2H_2O$$

$$H_2ZnO_2 + 2OH^- = ZnO_2^{2-} + 2H_2O$$

?

△

1. What are the chemical properties of bases? Give examples and write ionic equations of reactions.
2. Write ionic equations for reactions between: (a) aluminium hydroxide and sulphuric acid solution, (b) potassium hydroxide solution and iron(III) chloride, (c) iron(III) hydroxide and nitric acid solution, (d) calcium hydroxide and copper(II) sulphate solutions (consult solubility table).
3. What are the chemical properties of acids? Give equations of reactions to illustrate each property. Write molecular and ionic reaction equations.
4. Write molecular and ionic equations for the reactions of sulphuric acid with (a) aluminium, (b) zinc oxide, (c) calcium hydroxide, (d) barium chloride (consult solubility table).
5. How can the amphoteric properties of a given hydroxide be proved experimentally?

Salts. According to the theory of electrolytic dissociation, salt is an electrolyte whose aqueous solution contains the ions of metal and of acid residue.

Salts can enter exchange reactions with acids, alkalis, and salts.

1. *Aqueous solutions of salts react with strong acids to form new salts and acids* if at least one of the reaction products is insoluble either in water or in the newly formed acid (precipitate), or if it is liberated as a gas.

When concentrated sulphuric acid is added to crystals of sodium chloride, hydrogen chloride is evolved. When the mixture is heated slightly, sodium hydrogen sulphate is obtained:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl\uparrow$$

The ionic equations of the reaction are

$$Na^+ + Cl^- + H^+ + HSO_4^- = Na^+ + HSO_4^- + HCl\uparrow$$

$$H^+ + Cl^- = HCl\uparrow$$

Such reactions are used for the preparation of volatile acids from their salts.

If an insoluble salt is formed, even a weak nonvolatile acid can displace a strong volatile acid from its salt:

$$3AgNO_3 + H_3PO_4 = Ag_3PO_4\downarrow + 3HNO_3\uparrow$$

The ionic equation of this reaction is

$$3Ag^+ + 3NO_3^- + 3H^+ + PO_4^{3-} = Ag_3PO_4 \downarrow + 3HNO_3 \uparrow$$

2. *Aqueous solutions of salts react with alkalis to form a new salt and a base* if at least one of the reaction products is insoluble.

Consider the reaction of the formation of an insoluble salt:

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 \downarrow + 2NaOH$$

The ionic equations of this reaction are

$$2Na^+ + CO_3^{2-} + Ca^{2+} + 2OH^- = CaCO_3 \downarrow + 2Na^+ + 2OH^-$$
$$Ca^{2+} + CO_3^{2-} = CaCO_3 \downarrow$$

An insoluble base is formed in the following reaction

$$FeSO_4 + 2KOH = Fe(OH)_2 \downarrow + K_2SO_4$$

The ionic equations of the reaction are as follows:

$$Fe^{2+} + SO_4^{2-} + 2K^+ + 2OH^- = Fe(OH)_2 \downarrow + 2K^+ + SO_4^{2-}$$
$$Fe^{2+} + 2OH^- = Fe(OH)_2 \downarrow$$

3. *Aqueous solutions of salts react with one another to form two new salts* if at least one of the salts formed is insoluble in water.

Consulting the Table of Solubility it is easy to determine which salt solutions can be reacted to precipitate the wanted salt.

Suppose we have to prepare lead(II) sulphate. Consult reference tables to find out that lead(II) nitrate and sodium (or potassium) sulphate are the required soluble salts:

$$Pb(NO_3)_2 + K_2SO_4 = PbSO_4 \downarrow + 2KNO_3$$

The ionic equations are

$$Pb^{2+} + 2NO_3^- + 2K^+ + SO_4^{2-} = PbSO_4 \downarrow + 2K^+ + 2NO_3^-$$
$$Pb^{2+} + SO_4^{2-} = PbSO_4 \downarrow$$

All the considered exchange reactions that involve salts occur without alteration of the oxidation number of elements. But salts can also be involved in oxidation-reduction reactions.

4. *Metals contained in salts can be replaced by other more active metals in aqueous solutions of salts.*

Place a cleaned iron nail in a solution of copper chloride: a reddish deposit of copper will soon appear on the surface of the nail

$$Fe + CuCl_2 = Cu + FeCl_2$$

The ionic equations of this reaction are

$$Fe^0 + Cu^{2+} + 2Cl^- = Cu^0 + Fe^{2+} + 2Cl^-$$
$$Fe^0 + Cu^{2+} = Cu^0 + Fe^{2+}$$

?
△

1. What are the chemical properties of salts? Give molecular and ionic equations of reactions to illustrate each property.
2. Write molecular and ionic equations for reactions between (a) magnesium sulphate and barium chloride, (b) copper(II) chloride and potassium hydroxide, (c) sodium phosphate and aluminium nitrate, (d) potassium carbonate and calcium chloride, (e) zinc nitrate and sodium carbonate. (Consult the Table of Solubility.)
3. How can (a) copper(II) nitrate, and (b) copper(II) hydroxide be obtained from copper(II) oxide? Write molecular and ionic equations for reactions.
4. Write molecular and ionic equations for reactions by which (a) zinc chloride and (b) zinc sulphate are obtained.
5. Give examples of oxidation-reduction reactions which can also be regarded as (a) addition, (b) decomposition, and (c) substitution reactions.
6. Give examples of (a) addition and (b) decomposition reactions that cannot be regarded as oxidation-reduction reactions.

1.10 Hydrolysis of Salts

Negligibly small (and equal) amounts of H^+ and OH^- ions are formed during dissociation of water. Solutions in which the concentrations of H^+ and OH^- ions are equal (as in pure water) are called neutral; solutions in which the OH^- ions prevail are called alkaline; and those in which the hydrogen ions H^+ predominate are called acid solutions.

Solutions of bases are alkaline, and of acids, acid. One can suppose that a solution of any salt is neutral because it can be regarded as the product of neutralization of alkali by acid. In order to check this conjecture pour sodium chloride solution into one test tube, sodium carbonate solution into another, and aluminium chloride solution into the third test tube. Add litmus to each solution: sodium chloride solution alone proves to be neutral while the solution of sodium carbonate appears to be alkaline and that of aluminium chloride, acid. Solutions of the latter two salts contain unequal amounts of H^+ and OH^- ions: the amount of the OH^- ions is greater than of the H^+ ions in the sodium carbonate solution, while the solution of aluminium chloride has a greater amount of the hydrogen ions H^+. How can this fact be explained?

Consider reactions that may occur between ions contained in solutions of these salts.

Sodium carbonate (soda) Na_2CO_3 is formed by a weak acid H_2CO_3 and a strong base NaOH. Sodium carbonate is a strong electrolyte and it fully dissociates in an aqueous solution into the ions of sodium Na^+ and residue ions of carbonic acid CO_3^{2-}:

$$Na_2CO_3 = 2Na^+ + CO_3^{2-}$$

These ions are present in solution together with the ions into which the water molecules dissociate

$$H_2O \rightleftarrows H^+ + OH^-$$

Sodium cations may be attracted to the hydroxide ions but no strong bonds arise between them because sodium hydroxide is a strong electrolyte. The sodium ions and the hydroxide ions do not therefore undergo any conversion and remain in solution.

A strong bond arises, however, between the CO_3^{2-} and H^+ ions, and the ion HCO_3^- (the anion of the weak carbonic acid) is formed. The reaction of sodium carbonate with water can be expressed by the following ionic equations

$$2Na^+ + CO_3^{2-} + HOH \rightleftarrows HCO_3^- + 2Na^+ + OH^-$$

$$CO_3^{2-} + HOH \rightleftarrows HCO_3^- + OH^-$$

The net ionic equation shows that the interaction between the anion of the weak acid contained in the salt solution and water gives a greater amount of the hydroxide ions than of the hydronium ions. The aqueous solution of sodium carbonate, as well as a *solution of any other salt formed by a strong base and a weak acid, is alkaline (reacts alkaline).*

The exchange reaction between salts and water is called hydrolysis (from the Greek *hydor* water and *lysis* loosening, solution).

A question may arise, why HCO_3^- ions (rather than H_2CO_3 molecules) are formed during the hydrolysis of sodium carbonate. In order to answer this question it is necessary to remember that carbonic acid dissociates in an aqueous solution. The number of the HCO_3^- ions is greater than that of the CO_3^{2-} ions because the hydrogen ion is more strongly bonded with the dinegative ion CO_3^{2-} than with the uninegative ion HCO_3^-.

Let us discuss now why aluminium chloride solution $AlCl_3$ reacts acid. This salt is formed by a strong acid HCl and a weak base $Al(OH)_3$. When the salt is dissolved in water it dissociates

$$AlCl_3 = Al^{3+} + 3Cl^-$$

The Al^{3+} cations are attracted by the hydroxide ions that are present in water and can form strong bonds with them. Conversely, when the chloride ions Cl^- are attracted by the hydronium ions, no strong bonds arise: hydrochloric acid is a strong electrolyte and it completely dissociates into ions. The following reaction occurs in the solution:

$$Al^{3+} + 3Cl^- + HOH \rightleftarrows Al(OH)^{2+} + 3Cl^- + H^+$$

$$Al^{3+} + HOH \rightleftarrows Al(OH)^{2+} + H^+$$

The OH^- ions are no longer attached to the $Al(OH)^{2+}$ ion to form $Al(OH)_2^+$ and $Al(OH)_3$ because the $Al(OH)^{2+}$ ion is more stable.

The equations show that the cation of a weak base reacts with water to give greater amount of the hydronium ions than of the hydroxide ions. The solution of aluminium chloride, and a *solution of any other salt formed by a weak base and a strong acid, reacts acid.*

The experiment described at the beginning of this section shows that sodium chloride solution reacts neutral, i.e. it does not undergo hydrolysis. This is quite correct because sodium chloride, like any other salt formed by a strong acid and a strong base, dissociates into ions that cannot form strong bonds with the hydrogen ions or with the hydroxide ions. Like pure water, the solution of such a salt therefore contains equal amounts of the H^+ and OH^- ions.

If the composition of a salt indicates that it can be hydrolyzed, it is necessary to remember that the salt should be soluble in water. The following would also hold, as a rule: (1) one molecule of water reacts with each metal ion (for salts of weak bases) or with the acid residue ion (for salts of weak acids); (2) the reactions of hydrolysis are reversible.

Let us show how the reaction of hydrolysis can be predicted, and its equation determined, using the reaction of hydrolysis of zinc sulphate by way of illustration. This salt is formed by a strong acid (sulphuric) and a weak base (zinc hydroxide). Only the metal ions of zinc alone should therefore be involved in the reaction. The left part of the equation is $Zn^{2+} + H_2O$. The hydroxide ion is eliminated from the water molecule and is attached to the zinc ion during the reaction. The $Zn(OH)^+$ is formed:

$$Zn^{2+} + H_2O \rightleftarrows Zn(OH)^+ + H^+$$

The hydrogen ions H^+ are accumulated in solution, which reacts acid.

In addition to soda Na_2CO_3, soaps (salts of weak organic acids) which hydrolyze to form a weak alkaline medium are used in the home. The hydrolysis of these salts accounts for their washing properties.

?
△

1. Make out ionic equations for hydrolysis of (a) copper(II) sulphate, (b) potassium sulphide, (c) lithium phosphate Li_3PO_4, (d) ferrous chloride, (e) aluminium sulphate, and (f) calcium sulphide. What is the reaction of the solution in each particular case?
2. Why is baking soda used to lower acidity of the gastric juice? Test baking soda, washing soda, and soap for their hydrolysis. Use phenolphthalein as an indicator.

2

Nitrogen Subgroup

2.1

Position of the Elements of the Nitrogen Subgroup in the Periodic System of Chemical Elements and the Structure of the Atoms of These Elements

We have already become acquainted with typical nonmetals: the elements of the main subgroup of the seventh group of the periodic system of chemical elements (halogens), and the elements of the main subgroup of the sixth group (oxygen, sulphur, selenium, and tellurium). Let us continue our study of the chemical elements. Consider the nonmetals of the 5th group that are placed in its main subgroup. The outer electron layer of these atoms contains five electrons, namely two paired *s* electrons and three unpaired *p* electrons.

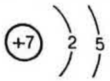
Three electrons are needed to complete the outer electron layers in the atoms of elements in the main subgroup of the 5th group (nitrogen, phosphorus, arsenic, antimony, and bismuth). The maximum number of electrons that can be eliminated from the atoms of these elements is therefore five, while the number of electrons that can be added to them is three. If five electrons are removed from the atom of a nonmetal, the chemical element shows a positive oxidation number, and if three electrons are added to its atom the element exhibits the negative oxidation number.

These properties of the atoms of the considered nonmetals determine the composition of their higher oxides and compounds with hydrogen (hydrides): the former have the formula $R_2^{5+}O_5^{2-}$, e. g. N_2O_5, nitrogen(V) oxide, P_2O_5, phosphorus(V) oxide; while the latter have the general formula $H_3^{+}R^{3-}$, e. g. NH_3, ammonia, and PH_3, hydrogen phosphide*.

Nitrogen and phosphorus are the most important nonmetals of the 5th group.

Nitrogen

Chemical symbol N; atomic number 7; atomic weight 14.
The structure of the atom:



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* The symbol of the element giving off the electrons is, by way of exception, written second in the formulas of these compounds.

2.2 Physical Properties of Nitrogen

The molecule of free nitrogen N_2 consists of two atoms connected by three pairs of shared electrons. This is described by the electron formula $:\mathrm{N}\vdots\vdots\mathrm{N}:$ or the structural formula $N \equiv N$.

The molecular weight of nitrogen (28) is only slightly smaller than the mean molecular weight of air (29), and nitrogen is therefore only slightly lighter than air.

The crystal lattice of nitrogen is molecular but the mutual attraction of the nitrogen molecules is so weak that nitrogen can be liquefied and crystallized only at very low temperatures. The boiling point of liquid nitrogen is lower than that of liquid oxygen. When liquid air is evaporated, mostly nitrogen is first evaporated. This phenomenon is used in industry to separate nitrogen and oxygen from air.

Nitrogen is sparingly soluble in water; its solubility is actually lower than that of oxygen.

We are in contact with free nitrogen throughout our lives. Nitrogen is the main component of air and its volume fraction in air is 4/5. It is easy to conclude that nitrogen is a colourless and odourless gas. It has no taste and is harmless to man. Animals die in an atmosphere of pure nitrogen only because of the lack of oxygen.

From our course of biology we know that nitrogen is a very important element which is vital for life on the Earth. Some people maintain that nitrogen is more valuable than the rarest noble metals. It is a component part of proteins, the fundamental structural material of all living matter. The weight fraction of nitrogen in proteins is 18 per cent. It is also contained in other organic compounds such as chlorophyll, etc. A deficient amount of nitrogen retards the growth of plants: the leaves first turn pale green and then yellow, and photosynthesis ceases.

?
△

1. Name the physical properties of nitrogen that you know.
2. Prove the molecular formula of nitrogen by considering its density relative to air (0.95).
3. When tap water is warmed in a beaker, gas bubbles appear on its walls. Explain. What is the difference between the composition of gas in these bubbles and in the atmospheric air?

2.3 Chemical Properties of Nitrogen

The triple bond in the nitrogen molecule accounts for its greater strength compared with oxygen and fluorine the elements that come after nitrogen in the periodic table. The more strongly atoms are bonded in the molecule of a nonmetal, the more difficult it is for it to enter chemical reactions.

Fill a flask with nitrogen, light a hydrogen torch, and lower it into the flask: the torch goes out. Now try burning charcoal, phosphorus, or sulphur: the flame is also extinguished. In these conditions nitrogen does not react with hydrogen, carbon, sulphur or phosphorus.

Nitrogen is located in the right upper corner of the periodic table. It only comes third (after fluorine and oxygen) with respect to its electronegativity: it acts as an electropositive element only with respect to fluorine and oxygen. In compounds with all other elements, nitrogen exhibits a negative oxidation number. These compounds are called nitrides, e. g. $Mg_3^{2+}N_2^{3-}$ magnesium nitride. When magnesium burns in air magnesium nitride is formed along with magnesium oxide:

$$3Mg + N_2 = Mg_3N_2 + Q$$

Compounds containing the N^{3-} ions do not occur in nature. If nitrogen (not oxygen) were the most abundant element in the Earth's crust, the latter would mostly consist of nitrides rather than oxides. Hydrogen would not then fill depressions in the earth with its oxide, water, but would be contained in the atmosphere in the form of its compounds with nitrogen, ammonia NH_3. The atmosphere of the outer planets in the solar system (Jupiter, Saturn, and those farther away from the Sun) consists of ammonia.

Nitrogen can react with hydrogen

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + Q$$

to give ammonia, the compound in which the oxidation number of nitrogen is 3−.

Nitrogen reacts with oxygen as well

$$N_2 + O_2 \rightleftarrows 2NO - Q$$

We shall further discuss in more detail the conditions under which nitrogen can combine with hydrogen and oxygen.

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△

1. What are the chemical properties of nitrogen?
2. Compare the chemical properties of nitrogen with those of oxygen and fluorine. What regularity can be found in the changes of these properties in the transition from fluorine to nitrogen?
3. What is common in chemical properties of nitrogen and carbon dioxide? How do these gases differ?
4. Give formulas for compounds of nitrogen with two elements that, after oxygen, are the most abundant in the Earth's crust. Remember that these are elements with constant valency. Name these compounds.
5. Air containing hydrogen sulphide and water vapour was passed through sodium hydroxide solution and then through concentrated sulphuric acid and calcined copper shavings. What gases were absorbed by each substance and what is the final composition of the gaseous mixture thus treated?
6. How can nitrogen be isolated from air in the laboratory? Describe the experiment. What chemical property of nitrogen is illustrated by this experiment? Characterize the purity of nitrogen prepared in this way.

2.4 Reaction of Nitrogen with Hydrogen

The history of the reaction between nitrogen and hydrogen $N_2 + 3H_2 \rightleftarrows 2NH_3$ is remarkable. Many scientists tried to carry out this reaction during the course of the past century using all the chemical methods then available: they heated the initial substances, passed electric discharges through them, and tried various catalysts. But none of these attempts succeeded. Today we can easily explain their failure since we know that the nitrogen molecule is very stable. It was only early in the 20th century that theoretical chemistry explained the conditions under which this reaction might be realized.

Let us carry out this reaction in the laboratory using the apparatus shown in Fig. 2.1. Mix nitrogen and hydrogen in the ratio of 1:3. The volumes of the gases can roughly be measured out by counting the bubbles as the gases are passed through concentrated sulphuric acid. Gaseous mixture passes through a glass tube into a bottle containing phenolphthalein solution. First pass the gaseous mixture through an empty tube without heating. The experiment shows that the reaction does not occur at normal pressure and a temperature of 20–25 °C: phenolphthalein colour does not change. Now heat the nitrogen-hydrogen mixture in the tube: still no reaction occurs. Now let us try catalysts. Place powdered iron in the tube and pass the gaseous mixture through it again at normal temperature. The reaction does not occur. Heat the tube: the colour of phenolphthalein now changes. This indicates that ammonia is formed over the iron catalyst at elevated temperatures. The reaction is thus catalytic:

$$N_2 + 3H_2 = 2NH_3 + Q$$

The determination of concentration (by volume) of ammonia in the resultant gaseous mixture issuing from the gas-outlet tube shows that it does

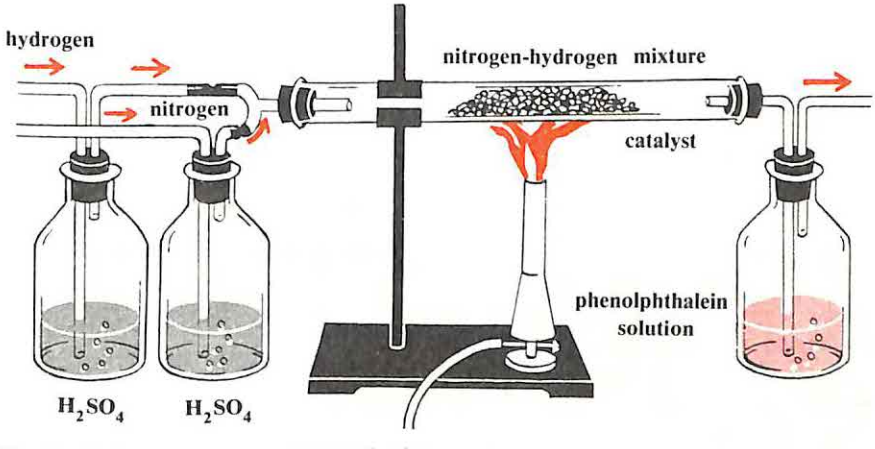


Fig. 2.1 Laboratory ammonia synthesis unit

not exceed 0.4 per cent at 400 °C, normal atmospheric pressure in the presence of catalyst. The concentration of ammonia in the mixture does not increase if we keep the mixture in the reaction tube for a longer time.

We already know that this happens because of the reversibility of the reaction. In order to prove it experimentally carry out the reverse reaction:

$$2NH_3 = N_2 + 3H_2 - Q$$

Pass ammonia through the tube filled with the same catalyst and at the same temperature. Ammonia almost completely decomposes into the starting nitrogen and hydrogen. The issuing gas can be lit by a match: hydrogen burns in air. Measurements show that the volume percentage of ammonia in the resultant mixture is the same as in the mixture obtained during synthesis of ammonia, i.e. 0.4 per cent. It indicates that the equilibrium at 400 °C and under atmospheric pressure is shifted toward nitrogen and hydrogen.

The reaction between nitrogen and hydrogen is exothermic. The equilibrium therefore shifts toward the formation of ammonia when temperature is lowered. But the reaction is known to occur only at elevated temperatures. Does the pressure affect the equilibrium of this reaction?

We cannot carry out reactions at elevated pressures at a school laboratory, but the data obtained by investigators show that the equilibrium of this reaction depends on both temperature and pressure (see Table 2.1). The tabulated data show that the equilibrium of the ammonia synthesis is shifted toward the formation of ammonia at elevated pressures. Pay attention to the changes in the volume of the gaseous mixture during the synthesis: the equation shows that the volume is halved.

Table 2.1

Concentration of Ammonia (in Per Cent by Volume) in a Mixture of Nitrogen and Hydrogen at Equilibrium (N_2 to H_2 Ratio, 1 : 3)

Temperature, °C	Volume percent of ammonia at various pressures, in MPa					
	10	30	100	150	200	350
400	25.12	47.00	79.82	88.54	93.07	97.73
450	16.43	35.82	69.69	84.07	89.83	97.18
500	10.61	26.44	57.47	data are not available		
550	6.82	19.13	41.16			

Equilibrium shifts according to the following general principles:

if the volume of the reaction system decreases during the reaction, the equilibrium is shifted toward the formation of the reaction products by increasing the pressure;

if the volume of the reaction system increases during the reaction, the equilibrium is shifted toward the formation of the starting substances by increasing the pressure.

The data given in Table 2.1 show that the equilibrium fails to be shifted completely toward the formation of ammonia even at very high pressures.

But perhaps the reaction can be made more effective if we use another catalyst for the synthesis of ammonia at higher rates and at temperatures lower than 400 °C? The solution of this problem will have a great industrial importance but such a catalyst has not yet been found although tens of thousands of different catalysts have been tried by investigators.

?
△

1. An equilibrium is established in the synthesis of ammonia. Suppose that 1 milliard of ammonia molecules form during 1 second in the reaction mixture. Calculate the number of ammonia molecules that are spent and of hydrogen and nitrogen molecules that are formed during this time. Fill in Table 2.2.

Table 2.2

Gas	Molecules spent	Molecules formed
NH_3	?	10^9
N_2	?	?
H_2	?	?

2. The dependence of equilibrium on temperature and pressure becomes more vivid when shown graphically. Draw two graphs. Let one graph show the variation of equilibrium output of ammonia with pressure at 400 and 550 °C, and the other graph, the dependence of output on temperature at 10 and 100 MPa.
3. Using the graph determine the equilibrium output of ammonia at 10 MPa and 200 °C.
4. How much hydrogen and nitrogen (in kg and litres) is needed to form 1 kg of ammonia at STP?
5. In what direction does the equilibrium shift in the reaction $2SO_2 + O_2 \rightleftarrows 2SO_3 + Q$ if the pressure increases?

2.5

Reaction of Nitrogen with Oxygen

We live on the 'bottom' of the air ocean that consists mostly of nitrogen and oxygen and in normal conditions no reaction occurs between them. But during thunderstorms, when lightning passes through the air, the following reaction occurs

$$N_2 + O_2 \rightleftarrows 2NO - Q$$

The reaction becomes possible because the temperature in the lightning is several thousand Celsius degrees.

The reaction by which nitrogen is oxidized to nitrogen(II) oxide is reversible and in accordance with the known principle the equilibrium shifts toward the formation of nitrogen(II) oxide when the temperature is raised. But even at very high temperatures (of about 2000 °C) the concentration of nitrogen(II) oxide in the equilibrium mixture is very small.

An artificial lightning is easy to obtain in the laboratory using the apparatus shown in Fig. 2.2. As an electric discharge passes through the air a little brown cloud is formed in the space between the electrodes. The smell

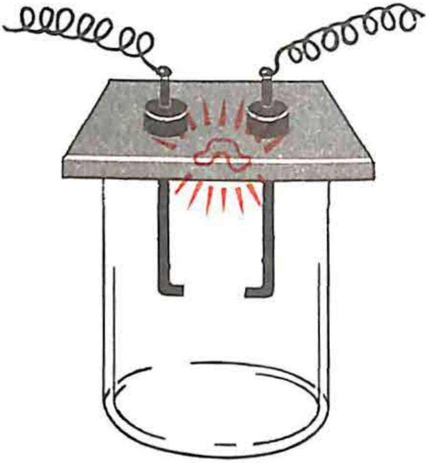


Fig. 2.2 Reaction of nitrogen with oxygen

is pungent. At high temperatures nitrogen combines with oxygen to form a colourless gas nitrogen(II) oxide NO, whose molecules combine at room temperature with another oxygen to form another oxide of nitrogen(IV), NO_2. This is a brown gas with the specific pungent odour.

?
△

1. Can the reaction of nitrogen oxidation by oxygen be called burning of nitrogen? Reason your answer.
2. How do the changes in temperature and pressure affect the equilibrium of the reaction of nitrogen oxidation by oxygen?
3. Does the exhaust gas of car internal combustion engines contain nitrogen(II) oxide? Reason your answer.

2.6 Ammonia

Volatile compounds with hydrogen are characteristic of all nonmetals. The volatile hydride of nitrogen is ammonia NH_3. This is a colourles gas with a pungent odour, almost two times lighter than air. At normal temperatures but under increased pressures ammonia is liquefied. When liquid ammonia evaporates, it absorbs much heat. This phenomenon is utilized in refrigerators.

Let us consider the reaction of ammonia with oxygen. In the simple apparatus shown in Fig. 2.3 ammonia and oxygen are supplied through narrow tubes. If we light the torch, ammonia burns with a blueish flame. Free nitrogen and water vapour are formed during the burning of ammonia:

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O + Q$$

The reaction is irreversible and strongly exothermic. Mixtures of nitrogen with oxygen or air are explosive and therefore dangerous.

Ammonia can react with oxygen in a different way. If we pass oxygen or air through a hot solution of ammonia, and lower a platinum spiral into the

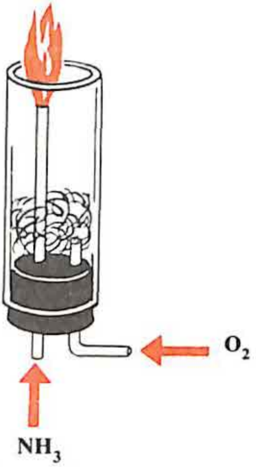


Fig. 2.3 Burning of ammonia

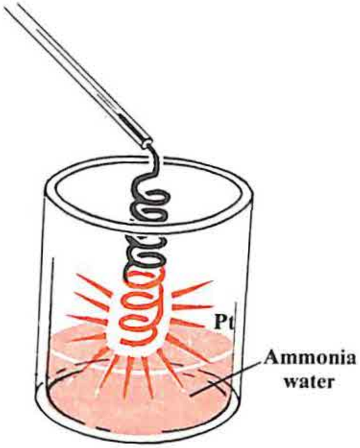


Fig. 2.4 Catalytic oxidation of ammonia

beaker without touching the liquid as shown in Fig. 2.4, the spiral will become white hot. This is because ammonia liberated from the solution reacts with oxygen on the platinum's surface to form nitrogen(II) oxide and water vapour:

$$4NH_3 + 5O_2 = 4NO + 6H_2O + Q$$

The reaction is irreversible as well. Platinum acts as a catalyst in this reaction. It becomes hot at the expense of the heat evolved during the reaction. Oxides of some metals, e. g. of iron and chromium, can also be used to catalyze the reaction.

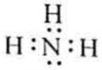
In studying the reaction of ammonia oxidation, we first dealt with an irreversible chemical reaction whose products can be varied by changing the conditions. If the reaction is conducted without any catalyst, nitrogen is the only reaction product; if the best catalysts are used, up to 98 per cent of ammonia can be oxidized to nitrogen(II) oxide while the remaining 2 per cent, to nitrogen.

Hydrides of nonmetals that we have already studied (hydrogen halides, hydrogen sulphide) dissociate in water to form hydronium ions and the ions of the acid residue. Ammonia also reacts with water during dissolution but in a different way.

Overturn a beaker containing ammonia into a dish filled with water: the vessel will soon be filled with water which indicates the good solubility of ammonia in water. A volume of water can dissolve up to 700 volumes of ammonia at normal temperatures. An aqueous solution of ammonia is called ammonia water.

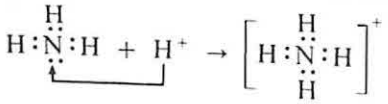
Let us test ammonia water for conductivity using the apparatus shown in Fig. 1.2. When the electrodes are immersed in ammonia water the lamp lights up. This indicates that the solution of ammonia in water contains ions.

What are these ions? Add a few drops of phenolphthalein or violet litmus to the solution: phenolphthalein turns crimson, and litmus blue (not red as is the case with solutions of hydrogen halides or hydrogen sulphide). We have thus detected the presence of the hydroxide ions OH^- in ammonia water. This ion might appear as a result of some reaction between ammonia and water. What reaction could it be? The electron-dot formula of ammonia is



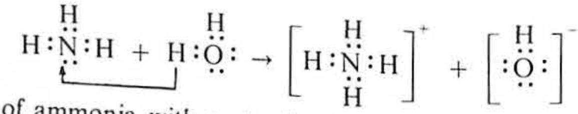
$$\mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot\cdot}{N}}:H}$$

Like the molecule of water, the ammonia molecule can attach the hydrogen ion, i.e. the proton, by attracting it with its free electron pair:



$$\mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot\cdot}{N}}:H} + \mathrm{H^+} \rightarrow \left[\mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{N}}:H}\right]^+$$

In this case the protons are eliminated from water molecules (one proton from each molecule):



$$\mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot\cdot}{N}}:H} + \mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot\cdot}{O}}:} \rightarrow \left[\mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{N}}:H}\right]^+ + \left[\mathrm{:\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot\cdot}{O}}:}\right]^-$$

The reaction of ammonia with water is the *donor-acceptor interaction*. The ammonia molecule is the *donor* and the proton eliminated from the water molecule is the *acceptor*.

Why do the bonds between oxygen and hydrogen in the water molecule break while the bonds between nitrogen and hydrogen in the ammonia molecule do not? This happens because the charges of the nitrogen and oxygen nuclei are different: the charge of the nitrogen nucleus is + 7 and of the oxygen nucleus + 8. The nucleus of the oxygen atom has a higher positive charge and repels the protons stronger than the nitrogen nucleus. The bond between the hydrogen and oxygen atoms can therefore be broken more easily.

The hydroxide OH^- and NH_4^+ ions are thus formed. The latter ion is called the *ammonium ion*.

The reaction between ammonia and water can be shown by a simplified equation

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

The reaction is reversible. Only a small proportion of dissolved ammonia is present in solution in the form of the ammonium ions while the greater part is contained as NH_3 molecules. Ammonia water therefore smells of ammonia: when exposed to air and heat it liberates the dissolved ammonia.

The nitrogen atom forms three covalent bonds in the ammonia molecule and four in the ammonium ion. As we know, these four bonds were formed by different mechanisms: three were formed by pairing the electrons of the nitrogen atom with the electrons of the attached hydrogen atoms, while the fourth bond was formed by attaching the proton to the free electron pair of the nitrogen atom. But despite their different origin, all four bonds in the ammonium ion are absolutely equivalent and the ion has therefore the configuration of a regular triangular pyramid (tetrahedron).

The ability of the ammonia molecule to attach the proton should show not only in its reaction with water but also in other properties of ammonia. One may expect that the attachment of protons will be especially easy during the reaction of ammonia with acids, substances in which the hydrogen atoms are loosely connected with the acid residues.

Carry out the following experiment. Dip a glass rod in concentrated ammonia water and another glass rod in concentrated hydrochloric acid. Bring the glass rods close to each other: a heavy white smoke appears. The smoke consists of minutest crystals of ammonium chloride:

$$NH_3 + HCl = NH_4Cl$$

Ammonia reacts with acids to form salts.

In medicine and in the home we use ammonia solution in the form of ammonia water or sal ammoniac (ammonium chloride). Ammonia is also used as a household cleaning fluid. Sal ammoniac is given as a stimulant in faints. Concentrated ammonia water is used as a liquid fertilizer in agriculture.

?
△

1. Describe the physical properties of ammonia.
2. Describe the reactions of (a) burning and (b) catalytic oxidation of ammonia and give the reaction equations. Write equations of the oxidation-reduction reactions with an electron balance.
3. Write the equation of copper reduction from copper(II) oxide by ammonia. Explain the reaction from the standpoint of the electron theory. Which compound is oxidized and which reduced in the reaction?
4. What is an aqueous solution of ammonia? What molecules and ions are contained in it? How are these ions formed?

5*. A proton is added to the nucleus of a carbon atom in a methane molecule CH_4. What molecule will thus be formed?

6. How can ammonia be poured from one beaker to another without being mixed with air? Use a strip of paper impregnated with phenolphthalein solution to observe the results of the experiment.

2.7

Salts of Ammonium

Like all salts, ammonium salts are composed of ions and crystallize in the ionic lattice, e. g. ammonium nitrate consists of NH_4^+ and NO_3^- ions. Ammonium salts are crystalline substances that are very similar to the corresponding salts of the alkali metals, especially those of potassium, because the radius of the ammonium ion is close to that of the potassium ion. Most physical properties of ammonium salt solutions are similar to those of potassium salts (with the same molar concentration).

Like the salts of the alkali metals, all ammonium salts are soluble in water and are strong electrolytes, i. e. fully dissociate in aqueous solution into ions:

$$NH_4NO_3 = NH_4^+ + NO_3^-$$

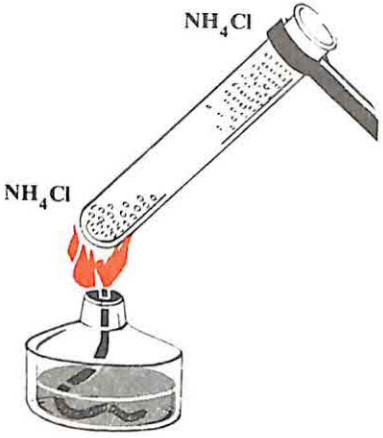


Fig. 2.5 Sublimation of ammonium chloride

Ammonium salts must therefore enter exchange reactions with other salts. If we add silver nitrate solution to the solution of ammonium chloride, silver chloride precipitates and ammonium nitrate remains in solution:

$$NH_4Cl + AgNO_3 = AgCl\downarrow + NH_4NO_3$$

Ammonium nitrate can be isolated as crystals if silver chloride is separated by filtration and the remaining solution is evaporated.

Ammonium ions are not destroyed in exchange reactions between salts, but pass as whole units into a newly formed salt.

Ammonium salts react with alkalis differently from other salts. When an alkali is added to a solution of any ammonium salt (or to a solid ammonium salt) one might expect that ammonium hydroxide should be formed:

$$NH_4Cl + NaOH = NH_4OH + NaCl$$

But ammonium hydroxide is unstable and it decomposes into water and ammonia

$$NH_4OH = NH_3\uparrow + H_2O$$

The reaction of an ammonium salt with an alkali therefore gives a new salt, ammonia, and water:

$$\begin{aligned} NH_4Cl + NaOH &= NaCl + NH_3\uparrow + H_2O \\ NH_4^+ + OH^- &= NH_3\uparrow + H_2O \end{aligned}$$

The equation shows the following general property of ammonium salts: all ammonium salts are destroyed by alkalis to evolve ammonia. This property is used in the laboratory for preparation of ammonia and for identification of ammonium salts.

Place an unknown salt (or its solution) in a test tube, add alkali, and heat. The liberated ammonia, if any, can be detected by its acrid odour. If wetted litmus paper is brought to the mouth of the test tube, the presence of ammonia will be detected by a change of litmus colour. The liberation of ammonia indicates the presence of ammonium ions in the solution.

The ammonium ions can be destroyed also by heating ammonium salts. When crystalline ammonium chloride NH_4Cl is heated in a test tube it sublimes like iodine (Fig. 2.5). But sublimation of iodine is a physical phenomenon while sublimation of ammonium chloride is a reversible chemical reaction. When heated, ammonium chloride decomposes into hydrogen chloride and ammonia

$$NH_4Cl = NH_3 + HCl$$

Ammonia and hydrogen chloride are volatile, but as they contact the cold walls of the test tube, they combine again

$$NH_3 + HCl = NH_4Cl$$

?

△

1. What methods of preparing ammonium salts do you know? Give reaction equations.
2. Describe the general (a) physical and (b) chemical properties of ammonium salts. Give the corresponding reaction equations.
3. How can ammonium chloride be distinguished from ammonium sulphate experimentally?
4*. A nitrogen compound is given. The ratio of nitrogen, sulphur, hydrogen and oxygen in its molecule is 1 : 1 : 5 : 4. This compound reacts with alkali to give ammonia, and with barium chloride to give a precipitate insoluble in hydrochloric acid. Name the compound. What is the colour of litmus in its solution? Prove your answer by ionic equations of the reactions.
5. A mixture of sand and ammonium chloride is given. Separate the mixture using (a) water or (b) a heater. Write the reaction equations.
6. Hold a strip of paper wetted with hydrochloric acid over paper wetted with ammonia water: dense smoke is formed. If the papers are changed places, the smoke is less dense. Explain.

2.8

Manufacture of Ammonia

Early in this century scientists undertook a physicochemical study and sought for an industrial method to 'fix' molecular nitrogen. Synthesis of nitrogen(II) oxide and ammonia were the main concern of the investigators.

Nitrogen is oxidized at high temperatures but the yield of nitrogen oxide is low. Much energy is required to heat air. Preparation of nitric acid and nitrates from nitrogen(II) oxide is difficult because of the low concentration of nitrogen(II) oxide in the gaseous mixture. The industrial plants that had then been built for the oxidation of nitrogen were closed down in the 1920s. The search for more advantageous methods of synthesizing nitrogen(II) oxide still continues.

It has been proved economically efficient to fix nitrogen not with oxygen but with hydrogen. At the present time tens of millions of tons of ammonia are being synthesized every year. Ammonia has become a universal raw material in the manufacture of other nitrogen-containing chemical products.

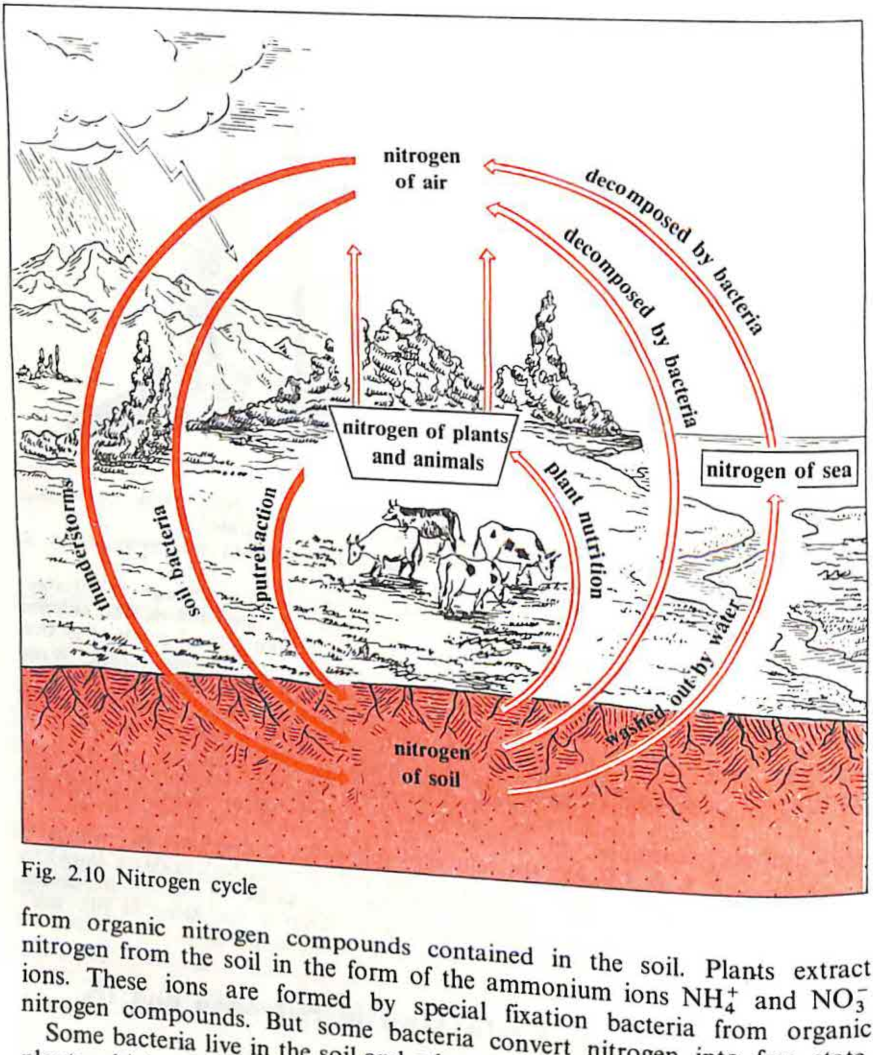


Fig. 2.10 Nitrogen cycle

from organic nitrogen compounds contained in the soil. Plants extract nitrogen from the soil in the form of the ammonium ions NH_4^+ and NO_3^- ions. These ions are formed by special fixation bacteria from organic nitrogen compounds. But some bacteria convert nitrogen into free state.

Some bacteria live in the soil and others in the root nodules of leguminous plants which assimilate free nitrogen to convert it into organic compounds.

Soils are enriched with nitrogen by rain water whose drops contain nitric acid formed during thunderstorms.

This nitric acid is converted into nitrates in the soil.

The extraction of combined nitrogen from the soil is thus compensated for by the natural processes which replenish the store of fixed nitrogen. The cycle of nitrogen in nature is thus completed (Fig. 2.10).

Cultivated plants take up more nitrogen than is replenished by natural processes and by fertilization of the soil by manure. As agriculture develops, the problem of nitrogen deficiency becomes more pressing. In the first half of the last century it was established that mineral nitrogen compounds are necessary for the growth of plants. Chile niter came into use in many countries as a fertilizer. But this source of fixed nitrogen could not meet the growing demand for nitrogen fertilizers, and by the end of the last century the scientists began a search for fixation of atmospheric nitrogen to produce fertilizers. This problem was only solved a few decades ago and now many industrial plants produce mineral fertilizers.

Nitrogen compounds are used in large amounts in organic synthesis in the manufacture of dyes, explosives, etc. Ammonia is known to be widely used in refrigeration technique. The inertness of nitrogen is utilized in all cases where it is necessary to prevent undesirable chemical reactions. Nitrogen is used to fill electric bulbs, and to create a neutral atmosphere for the storage and pumping of inflammable fluids.

△

1. Antoine Lavoisier suggested that nitrogen be called 'azote' (from the Greek negative prefix *a* and *zoe* life) to show that this gas does not support life. Remember the history of chemistry and try to explain Lavoisier's suggestion for how can nitrogen be called 'azote', when life is impossible without it?
2. Later the gas was given the name of 'nitrogen' while the name proposed by Lavoisier has survived in French and Russian. Try to explain the word 'nitrogen'.
3. The origin of Chile niter has not been so far explained since we know the chemical properties of nitrogen and its compounds, and have studied the nitrogen cycle, let us try to formulate our own hypothesis about the origin of the Chile niter deposit.
4. Fig. 2.10 shows the nitrogen cycle in more detail than is given in the text. What new processes have been added to the nitrogen cycle in the figure?
5. Remember the properties of nitrogen and indicate two methods by which atmospheric nitrogen could be fixed in compounds at chemical plants. Write equations for the reactions by which calcium nitrate is prepared by each method.

2.13 Chemical Reactions Used in the Manufacture of Nitric Acid

Before the synthesis of ammonia had been mastered, nitric acid was prepared by the action of sulphuric acid on Chile niter. The acid was only used in the manufacture of explosives, dyes, and some other chemical products. Now nitric acid is prepared from synthetic ammonia and is mainly converted into nitrogen fertilizers.

How can nitric acid be prepared from ammonia?

Several reactions should be carried out one after another. Each of these reactions is already known to us. They are as follows:

$$4NH_3 + 5O_2 = 4NO + 6H_2O + Q \quad (1)$$

$$2NO + O_2 \rightleftarrows 2NO_2 + Q \quad (2)$$

$$3NO_2 + H_2O = 2HNO_3 + NO + Q \quad (3)$$

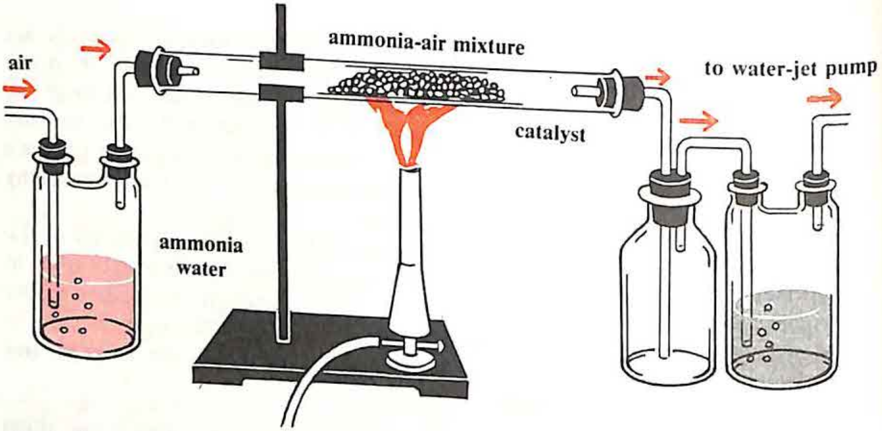


Fig. 2.11 Laboratory unit for oxidation of ammonia

Let us prepare nitric acid from ammonia in the apparatus shown in Fig. 2.11. In order to obtain an ammonia-air mixture, pass a jet of air through ammonia water. Place a small portion of granular catalyst (metal oxide) in a horizontal tube and pass the air-ammonia mixture through it. In order to initiate the reaction the catalyst should be heated. The burner may later be removed since the temperature required for the reaction will be maintained by the heat that evolves during the reaction.

As the gaseous mixture leaves the tube it enters a bottle where nitrogen (II) oxide is oxidized by the oxygen remaining in the gaseous mixture. The gas then enters a two-neck bottle where nitrogen (IV) oxide reacts with water to form an aqueous solution of nitric acid.

In industry ammonia is oxidized by a different method. Pure ammonia is mixed with air cleaned of extraneous impurities and the mixture is passed over a platinum-rhodium catalyst. Gas obtained by this reaction (1) is cooled. Nitrogen (IV) oxide obtained in reaction (2) is delivered to towers whose design is similar to that described in the manufacture of sulphuric acid, except that chromium-nickel steel resistant to nitric acid and nitrogen oxides is instead used for the construction of the towers.

Since the rate of oxidation of nitrogen (II) oxide to nitrogen (IV) oxide increases sharply with increasing pressure, the reaction is carried out under elevated pressure (to 1 MPa). The volume of the apparatus is much smaller than in earlier units in which the process was carried out under normal pressure.

The reversible reaction of nitrogen (IV) oxide with water gives dilute nitric acid with a concentration of 50–60%. This acid is used in the manufacture of fertilizers.

How can the concentrated (e. g. 98%) acid that is required for the manufacture of dyes and other organic substances be prepared?

One can guess that the equilibrium

$$4NO_2 + O_2 + 2H_2O \rightleftarrows 4HNO_3 + Q$$

should be displaced by increasing pressure. In fact, concentrated nitric acid is produced in industry by this method: the reaction is carried out at a pressure of about 5 MPa.

Another method can also be used: concentrated sulphuric acid is added to dilute nitric acid and the mixture is heated. Only nitric acid is evaporated, while water and sulphuric acid remain liquid.

At some plants producing nitric acid one can still observe the discharge of flue gas coloured by nitrogen(IV) oxide: it is very difficult to completely trap nitrogen oxides because the rate of oxidation of nitrogen(II) oxide is very low due to its low concentration in the flue gas.

Nitrogen oxides are harmful to man and plants. Flue gases at modern plant are therefore heated and the nitrogen oxides are decomposed over catalysts, and only then are they discharged into the atmosphere.

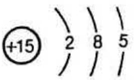
?
△

1. What is the difference between the method for preparing nitric acid in the laboratory and in industrial conditions?
2. What quantity of ammonia should be taken to prepare 1000 tons of anhydrous nitric acid, if the yield of nitrogen(II) oxide during contact oxidation of ammonia is 98%, and 99% of nitrogen(II) oxide are converted to nitric acid? Solve the problem without making out equations.

2.14

Phosphorus

The chemical symbol of phosphorus is P, its atomic number 15, the atomic weight 31. The diagram of the atom structure is



Phosphorus was first isolated in the free state in the form of a wax-like substance that shone in the dark. Hence the name *phosphorus*, which literally means 'light bringer' (Greek). Volatile compounds of phosphorus, which are formed when organic remains decay have the same property. This accounts for the rare phenomenon of will-o'-the-wisp (misleading or wandering lights), which has become the cause of the superstition about the wandering souls of the dead who leave their graves.

Phosphorus in the free state has several allotropic forms. In accordance with its structure, the atom of phosphorus can form three covalent bonds like nitrogen does, but while all three bonds in the molecule of nitrogen are used to bind the atoms together, in all the allotropes of phosphorus all atoms are bonded in pairs by only one bond. If a phosphorus atom combines with three other phosphorus atoms in this way, all three attached phosphorus atoms will have two unused valency units (Fig. 2.12*a*), i.e. each of these three phosphorus atoms will have two unpaired electrons. The unused valency units may form bonds between the phosphorus atoms themselves which then combine into a tetra-atomic molecule. The configuration of this molecule is the triangular pyramid (tetrahedron) shown in Fig. 2.12*b*. White phosphorus consists of these molecules. Its crystal lattice

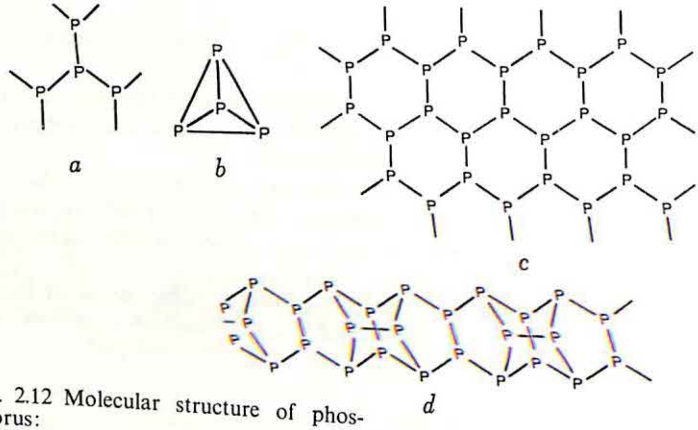


Fig. 2.12 Molecular structure of phosphorus:

a–a fragment that is present in molecules of all phosphorus allotropes; *b*–a molecule of white phosphorus; *c*–crystal lattice of black phosphorus; *d*–crystal lattice of red phosphorus

is thus molecular, composed of molecules bonded to one another by weak intermolecular forces. White phosphorus is therefore volatile and has a low melting point like all the other substances that have a molecular lattice. It is almost insoluble in water but is readily soluble in many organic solvents. White phosphorus is poisonous.

Look at Fig. 2.12*a* again. The attached phosphorus atoms can combine through their free valency units not just with each other but with other additional phosphorus atoms. The consequent structures will not, however, be white phosphorus with its crystal lattice, but will be another allotropic modifications with atomic crystal lattices. Their structural formulas are shown in Fig. 2.12*c* (black phosphorus) and 2.12*d* (red phosphorus).

When exposed to light, or heated slightly in the absence of air, white phosphorus converts into the red allotrope. Red phosphorus is isolated as a brown-red powder and like all substances with atomic crystal lattices, it is nonvolatile and insoluble in any solvent. Red phosphorus is not poisonous. When heated strongly in the absence of air it turns back into white phosphorus. This conversion can be observed in the dark when we strike a match without lighting it. The match head leaves for an instant a shining trace on the match box. This is white phosphorus that shines in the dark.

In accordance with its position in the periodic table, phosphorus is

Table 2.3

III	IV	V	VI	VII	VIII
B	C	N	O	F	Ne
	Si	P	S	Cl	Ar

electronegative with respect to the metals and hydrogen and electropositive with respect to the nonmetals coming to the right and above phosphorus in the periodic table (oxygen included). Look at Table 2.3: the symbols of elements that are electronegative with respect to phosphorus are given in red.

Phosphorus reacts with metals to form phosphides, e. g. magnesium phosphide Mg_3P_2.

The radius of the phosphorus atom is larger than that of nitrogen. The attraction of the valency electrons by the phosphorus atom is therefore weaker, and phosphorus gains the missing electrons that are required to complete its outer layer with greater difficulty than does nitrogen. For this reason, the oxygen compounds of phosphorus (in which it is electropositive) are more stable than the oxygen compounds of nitrogen, while the hydrides (in which phosphorus is electronegative) are by contrast less stable than nitrogen compound with hydrogen (ammonia). Hydrogen phosphide PH_3 (phosphine) is so unstable that, in contrast to ammonia, it cannot be obtained by directly combining phosphorus and hydrogen.

Phosphorus's oxidation reactions by oxygen and other oxidants are very characteristic of the element. When it reacts with oxygen, it burns with a bright white flame to form a solid higher oxide P_2O_5 in the form of a white smoke:

$$4\overset{0}{P} + 5\overset{0}{O}_2 = 2\overset{5+}{P}_2\overset{2-}{O}_5$$

Red phosphorus can only burn after it has been ignited, while white phosphorus oxidizes in air at room temperature (it shines). Shining of white phosphorus during its slow oxidation is an example of the direct conversion of the inner chemical energy of a substance into radiation.

A mixture of red phosphorus with potassium chlorate $KClO_3$ explodes at the slightest friction or pressure:

$$\overset{0}{P} + K\overset{5+}{Cl}O_3 \rightarrow \overset{5+}{P}_2O_5 + K\overset{1-}{Cl}$$

(Write the electron equations for this reaction and put the proper coefficients.)

This chemical reaction occurs each time we strike a match. A mixture of potassium chlorate, with, for example, sulphur as the combustible material is contained in the match head, while red phosphorus is the component of the mixture on the striking side of the match box (Fig. 2.13). The man's most ancient need for fire has thus been solved by red phosphorus.

? 1. Describe the physical and chemical properties of red and white phosphorus. Red phosphorus is heated strongly in the left end of a bent evacuated tube (Fig. 2.14*a*) while its right end is cooled. What is collected in the right end?

△ 2. Describe the chemical properties of phosphorus according to its position in the periodic table.

3. Calculate the number of electrons in the outer layer of each phosphorus atom in the molecule of white phosphorus and in crystal lattices of black and red phosphorus.

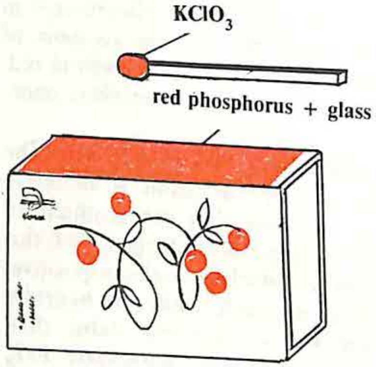


Fig. 2.13 Matches

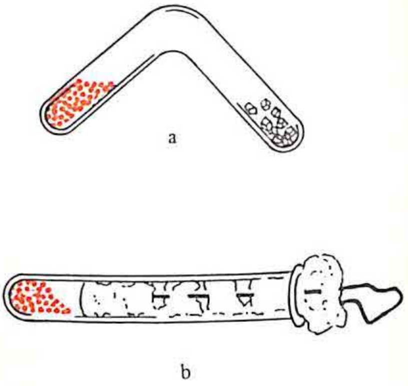


Fig. 2.14 Conversion of red phosphorus into white phosphorus

4. Write the formulas of (a) aluminium phosphide, (b) compound of sulphur and phosphorus, (c) compound of phosphorus and nitrogen, in which the electropositive element (its symbol in the formula goes first, as usual) has the highest oxidation number. Name these compounds.

■

5. Write the electron equation of the reaction, which occurs when a match is lit. The odour of what gas can be felt? Scrape off the striking surface (together with paper from the match, pack it in a test tube, and close with a cotton pad round which a thread is bound. Heat strongly (Fig. 2.14*b*), and pull energetically the cotton pad from the test tube by the thread: an interesting phenomenon is observed. Explain.

2.15

Oxygen Compounds of Phosphorus

When phosphorus burns, a dense white smoke is formed. It precipitates on the walls of the vessel in the form of a white powder. This is phosphorus(V) oxide P_2O_5. If water is added and the vessel is shaken, a cloudy liquid is first formed. The cloudiness soon resolves to give a clear solution which turns litmus red. The addition of water to phosphorus(V) oxide occurs in several steps.

A molecule of water is first attached to the phosphorus oxide molecule to give metaphosphoric acid. A simplified equation of this reaction is

$$P_2O_5 + H_2O = 2HPO_3$$

Another water molecule then attaches to metaphosphoric acid to give orthophosphoric acid, which is known simply as phosphoric acid

$$HPO_3 + H_2O = H_3PO_4$$

Phosphorus(V) oxide combines vigorously both with liquid water and with its vapour. This oxide is therefore used to dry gases.

Phosphoric acid H_3PO_4 is a solid substance readily soluble in water. Unlike nitric acid, phosphoric acid is nonvolatile. It dissociates in steps in solution:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- ; \quad H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-} ;$$
$$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-}$$

Being tribasic, phosphoric acid is weak.

During the dissociation of polybasic acids each subsequent hydrogen ion is eliminated with greater difficulty than the previous one because the charge of the anion increases and it becomes more difficult to overcome its attraction. Solutions of phosphoric acid, therefore, contain in addition to the molecules of H_3PO_4, many $H_2PO_4^-$ ions, very few HPO_4^{2-} ions, and a tiny number of PO_4^{3-} ions.

Phosphoric acid only reacts with metals that come before hydrogen in the electrochemical series. Its neutral salts are phosphates. Depending on the amount of the base added to the phosphoric acid solution, one, two, or three hydrogen atoms may be substituted for the metal atom

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O,$$
$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O,$$
$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$$

Therefore, phosphoric acid can react with one metal to give three different salts. If only one hydrogen atom is replaced by metal, while the other two hydrogens remain bonded to the acid residue in the univalent anion $H_2PO_4^-$, the salt is called dihydrogen or monobasic phosphate (*di* means two). If the metal substitutes for two hydrogen atoms in the acid molecule, only one hydrogen atom remains bonded to the acid residue to form the HPO_4^{2-} ion, the salt formed is called a hydrogen phosphate. If the metal is substituted for all the hydrogens in the acid molecule, the salt is simply called a phosphate. Examples of these salts are:

dihydrogen phosphates	NaH_2PO_4	$Ca(H_2PO_4)_2$,	$NH_4H_2PO_4$
hydrogen phosphates	Na_2HPO_4,	$CaHPO_4$,	$(NH_4)_2HPO_4$
phosphates	Na_3PO_4,	$Ca_3(PO_4)_2$	

Dihydrogen phosphates of all metals are readily soluble in water. Phosphates are insoluble in water (except those of the alkali metals) while hydrogen phosphates are intermediate in solubility between dihydrogen phosphates and neutral phosphates. All insoluble phosphates dissolve when strong acids are added because they are converted into acid salts, dihydrogen phosphates, e. g.:

$$Ca_3(PO_4)_2 + 4HNO_3 = Ca(H_2PO_4)_2 + 2Ca(NO_3)_2$$

The net ionic equation is

$$Ca_3(PO_4)_2 + 4H^+ = 3Ca^{2+} + 2H_2PO_4^-$$

Gaseous hydrides of arsenic and antimony (AsH_3 and SbH_3) are even less stable than hydrogen phosphide.

Higher oxides of the elements standing in the nitrogen subgroup have the general formula R_2O_5 and they give hydroxides with acid properties.

Arsenic acid H_3AsO_4 is very similar to phosphoric acid in its properties. Hydroxides corresponding to the higher oxides of antimony and bismuth have weak acid properties.

3 Mineral Fertilizers

We know from biology that various chemical elements play an important role in the life of plants. Some of us have used mineral fertilizers adding them to the soil. Remember what you know from theory and from your own practical experience and try to answer the following questions:

1. What substances are plants made of?
2. Of what elements are these substances composed?
3. Where do plants take the required nutrient substances?
4. Which mineral fertilizers do you know? What are they made up of and what do they do?
5. Which fertilizers have you seen used on farms? Which of them have you used yourselves? What do you know about their efficiency?

3.1 General Properties of Mineral Fertilizers and Land Improvement

The appropriate use of fertilizers can increase crop yields several times. However, what properties must a mineral fertilizer possess to meet the demands of agriculture adequately?

Mineral fertilizers are characterized by the concentration of nutrients they contain. The nutritive value of fertilizers is normally expressed by the percentage of nitrogen, phosphorus(V) oxide P_2O_5, potassium oxide K_2O, calcium oxide CaO, etc.

How can the percentage of K_2O and P_2O_5 in a mineral fertilizer be calculated? Let us determine the content of K_2O in potassium chloride. The fertilizer has no potassium oxide and the calculation is therefore only conventional. We act as follows:

(1) calculate the relative molecular weight of potassium chloride

$$M_r(\mathrm{KCl}) = 39 + 35.5 = 74.5$$

and the relative molecular weight of potassium oxide

$$M_r(\mathrm{K_2O}) = 78 + 16 = 94$$

(2) taking into consideration that one molecule of potassium chloride contains one potassium atom, and potassium oxide two potassium atoms, we divide the molecular weight of potassium oxide by twice the molecular weight of potassium chloride and multiply by 100. The result is the percentage of potassium oxide in potassium chloride:

$$\frac{94 \times 100\%}{2 \times 74.5} = 63.1\%$$

In order to determine the percentage of P_2O_5 in calcium dihydrogen phosphate $Ca(H_2PO_4)_2$ do the following:

(1) calculate the relative molecular weight of calcium dihydrogen phosphate

$$M_r[\mathrm{Ca(H_2PO_4)_2}] = 40 + 4 + 62 + 128 = 234$$

and the relative molecular weight of phosphorus(V) oxide

$$M_r(P_2O_5) = 62 + 80 = 142$$

(2) by taking into consideration the fact that there is an equal number of phosphorus atoms (two) in both molecules, divide the second number by the first and multiply the result by 100. The percentage of phosphorus(V) oxide in calcium dihydrogen phosphate is

$$\frac{142 \times 100\%}{234} = 60.7\%$$

The total output of mineral fertilizers is measured in millions of tons per year. The fertilizers must then be packed, transported by rail and other roads, kept at stores, and then added to the soil. All these labour-consuming operations are very costly, and so to reduce the expenses, the chemical industry should turn out *concentrated fertilizers*. For example, double superphosphate containing up to 48% of P_2O_5 should be produced instead of the simple superphosphate which contains up to 20 per cent of P_2O_5.

Many fertilizers, e. g. ammonium nitrate, potassium chloride, and superphosphate contain only one nutritive element, such as nitrogen, potassium, or phosphorus. These are *simple* fertilizers but plants normally need two, three or more elements. *Compound* (mixed) fertilizers containing various proportions of the nutritive elements (in accordance with the demands of particular plants) should therefore be produced. Some mixed fertilizers are substances containing two essentials, e. g. ammophose, which is a mixture of ammonium dihydrogen phosphate $NH_4H_2PO_4$ and ammonium hydrogen phosphate $(NH_4)_2HPO_4$. It is obtained by neutralizing phosphoric acid with ammonia.

Compound fertilizers containing the required proportions of the essential elements are prepared by mixing simple fertilizers. But not all fertilizers can be mixed because the components may react with each other, converting the nutrients into gases or into a less assimilable form.

When stored, some fertilizers can 'cake' to form large lumps or even solid heaps. They should be crushed before use and this is not an easy operation. The ability of some fertilizers to 'cake' often depends on how hygroscopic they are. Some fertilizers are so hygroscopic that they absorb moisture from relatively dry air. Ammonium nitrate (Norway saltpeter) is such a fertilizer. Fertilizers that cannot absorb water from air containing over 80 per cent of moisture, are called nonhygroscopic. Ammonium sulphate, for example, is nonhygroscopic. Granular fertilizers (granule size, 2-4 mm) have weaker tendency to caking and they are easier to add to soils. They are better assimilated by plants than are powdered fertilizers. Most fertilizers are therefore now produced in the form of granules.

Liquid fertilizers such as liquid ammonia, ammonia water (a 20-25% solution of ammonia in water), an aqueous solution of ammonium nitrate (containing dissolved ammonia), mixed fertilizers (containing nitrogen, phosphorus, potassium and microelements) are now widely used. Liquid fertilizers are cheaper than solid ones but special equipment is required for their introduction into soil.

?

1. Compare the concentration of nitrogen in the following substances: $NaNO_3$, $(NH_4)_2SO_4$, NH_4NO_3. Which of these substances can be called a concentrated fertilizer? What are the advantages of concentrated fertilizers?

△

2. Calculate the concentration of elements (calculating as their oxides) in the following substances: (a) double superphosphate, (b) pure potassium chloride, (c) sylvinite containing 28% of KCl and 72% of NaCl.
3. Calculate the concentration of nutritive elements in KNO_3, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$. Can ammonium nitrate be mixed with lime?
4. Calculate the concentration of nitrogen in liquid ammonia and 25 per cent ammonia water. Compare it with the concentration of nitrogen in solid fertilizers, for example, in potassium nitrate and ammonium nitrate.
5. Calculate the weight of ammonium nitrate, double superphosphate, and potassium chloride that should be added to soil for growing sugar beet if the normal requirements are 75 kg of N, 80 kg of P_2O_5, and 80 kg of K_2O per hectare.

3.2 Chemical Improvement of Soils

Soil improvement which is also known as melioration (the word derives from the Latin *melior* meaning better) *includes measures to improve the properties of soils*, such as the *reclamation of swamps*, *planting forests*, and *chemical methods.*

At each stage of the development of every type of plant there are optimum soil conditions favouring its growth. The reaction of soil solution is especially important. It depends on the concentration of the hydrogen ion in it.

Many of the soils in the Soviet Union are acid. However small the hydrogen ion concentration may be, it is several times higher than the hydrogen ion concentration in pure water or neutral solutions. Excess quantities of hydrogen ions are harmful to plants because the acidity of soil decreases the activity of the useful bacteria which live in the soil. Physical properties of such soils are unsatisfactory, their permeability to air and water is low. Acid soils may be improved by adding sufficient amounts of lime-containing substances.

In order to decrease the acidity of soils, crushed natural calcium carbonate is often used instead of calcium hydroxide. Calcium carbonate is insoluble in water but it reacts with hydrogen ions to form a soluble salt and carbon dioxide

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2O + CO_2$$

When the acidity decreases, the soil's structure changes as well: it becomes loose and permeable to air and water because the clay particles do not stick together.

A single liming of soil may continue its favourable effect on crop yields for a long period of time (to 15 years).

?
△

1. What is soil improvement (melioration)?
2. How do crop yields depend on soil acidity?
3. What does liming of soil mean? In what cases should lime be added to a soil and what effect does it have on crop yields? Write equations for the reactions that occur in the soil solution during liming.
4. Soils are considered to be strongly acidic if the concentration of hydrogen ions in the soil solution is at least 300 times more than that in pure water. What is the mass of the hydrogen ions contained in one litre of such a solution if the degree of water dissociation in normal conditions is 2×10^{-9}?

3.3 Nitrogen Fertilizers

Ammonia and nitric acid are used to manufacture various fertilizers. Urea (carbamide), $(NH_2)_2CO$, is a solid fertilizer in which the concentration of the nutrient is very high. This fertilizer does not absorb moisture from air at moderate humidity and does not therefore cake when stored. When added to soil, urea converts into ammonium carbonate:

$$(NH_2)_2CO + 2H_2O = (NH_4)_2CO_3$$

Urea is also used to supplement animal feeds. In the chemical industry it is one of the most important raw materials for the manufacture of plastics and many other products.

One of the most popular fertilizers is ammonium nitrate (Norway saltpeter). Its nitrogen content is greater than that of other solid fertilizers (except urea), but its disadvantage is that it cakes in storage. The disadvantage can, however, be overcome by granulating the fertilizer or by adding special substances that prevent the absorption of moisture. Ammonium nitrate should be kept in containers that isolate it from atmospheric moisture, for example in polyethylene bags.

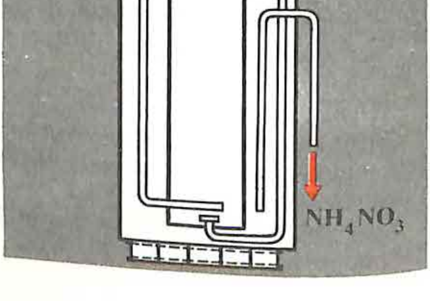


Fig. 3.1 Industrial unit for preparing ammonium nitrate

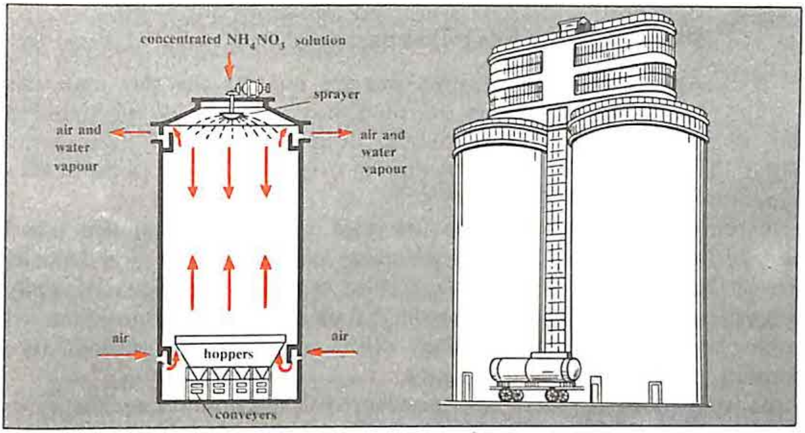


Fig. 3.2 Granulation tower: a longitudinal section and a general view

Ammonium nitrate is prepared by neutralizing nitric acid with ammonia. This is an exothermic irreversible reaction. The starting materials react completely when taken in amounts calculated from the chemical equation of the reaction.

An industrial apparatus used to manufacture ammonium nitrate is shown in Fig. 3.1. Dilute nitric acid and gaseous ammonia are fed continuously into the apparatus and ammonium nitrate emerges from it. Since the reaction is exothermic, the solution temperature rises, part of its water is evaporated, and the solution thus becomes more concentrated. The concentrated solution is then heated again and is converted into a melt which is granulated: the melt is fed at the top of high towers (Fig. 3.2) where it is atomized by a rotary sprayer. A countercurrent flow of air moves from the bottom of the tower to meet the falling drops of the melt, which thus cool to solidify into 1-3 mm granules.

?
△

1. Ammonium sulphate is obtained at coke plants by neutralizing ammonia contained in coke gas with dilute sulphuric acid. What quantity of sulphuric acid (as 100% H_2SO_4) is needed to obtain 1 ton of ammonium sulphate? (Disregard the loss.)
2. Compare raw materials needed to produce (a) ammonium nitrate, (b) ammonium sulphate, and (c) sodium nitrate. Which of these products are obtained from more accessible raw materials?
3. Why does granulated ammonium nitrate adsorb water vapour from air slower than the powdered fertilizer?
4. Make out a list of operations (in the order in which they follow in the flow-sheet) that are needed to produce (a) solid ammonium nitrate, (b) liquid nitrogen fertilizers. Which of these fertilizers requires smaller amounts of the starting materials? Which of them will be cheaper?

3.4

Phosphorus Fertilizers

Apatite and phosphorite ores are used as the raw materials for the manufacture of phosphorus fertilizers, phosphorus itself and all the phosphorus compounds. Both ores contain fluorapatite $Ca_5(PO_4)_3F$. The appatite ores are volcanic in origin, while the phosphorites are sedimentary rocks.

In prerevolutionary Russia phosphorites were mined from thin strata and the quality of the ores was poor. The discovery in the 1920s of rich deposits of apatite in the Kola Peninsula was therefore very important economically and a large plant was built there. The mined rock is separated into materials rich in phosphorus and nepheline tailings which are used in the manufacture of aluminium, soda, potash, and cement.

Thick phosphorite strata have been discovered in the South Kazakhstan in the Kara-Tau. The cheapest phosphorus fertilizer is phosphorite meal, which contains phosphorus as the water-insoluble calcium phosphate. Phosphorites are not therefore suitable for all soils or for all plants. The main bulk of the mined phosphorus ores is processed chemically into substances suitable for assimilation by all plants and in any soil. These are the water-soluble calcium phosphates: calcium dihydrogen phosphate $Ca(H_2PO_4)_2$ which is a component of superphosphate, a mixture of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ (ammophos), calcium hydrogen phosphate $CaHPO_4$ (precipitate) which is sparingly soluble in water but soluble in weak acids, etc.

Phosphoric acid is required for the manufacture of soluble phosphates. How can phosphoric acid be prepared from natural raw materials?

When calcium phosphate reacts with sulphuric acid, a calcium sulphate precipitate and an aqueous solution of phosphoric acid are obtained:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4\downarrow + Q$$

The reaction products are separated by filtration. Two substances are involved in this reaction, one liquid and the other solid. In order to increase the reaction rate, the solid should be crushed thoroughly and the reactants stirred during the reaction. The chemical reaction is exothermic and some of the water in the sulphuric acid is evaporated.

Phosphoric acid is also obtained in industry by another process. Natural phosphates react with carbon and silicon(IV) oxide at about 1 600°C to give gaseous phosphorus

$$Ca_3(PO_4)_2 + 5C + 2SiO_2 = 2P\uparrow + 5CO\uparrow + Ca_3Si_2O_7 - Q$$

The reaction is carried out in electric arc furnaces. The phosphorus is burned and the phosphoric acid is prepared by the reaction of the formed phosphorus(V) oxide with water.

The phosphoric acid prepared by this way is purer. Phosphoric acid can be obtained from phosphates of poor quality, but the method is only suitable where electricity is available.

A phosphorus fertilizer containing significant amounts of P_2O_5, is known as a double superphosphate and is obtained by the action of phosphoric acid on crushed natural phosphates:

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2$$

For more than hundred years, a simple superphosphate, formed by the action of sulphuric acid on natural calcium phosphate

$$Ca_3(PO_4)_2 + 2H_2SO_4 = Ca(H_2PO_4)_2 + 2CaSO_4$$

was the only phosphorus fertilizer.

The amount of sulphuric acid used to prepare simple superphosphate is smaller than that needed to make phosphoric acid from the same calcium phosphate. A mixture of calcium dihydrogen phosphate and calcium sulphate is thus prepared. It contains up to 20 per cent of P_2O_5.

? △

1. What is the concentration of fluorapatite in the apatite-nepheline rock mined at the Kola Peninsula if the concentrated rock contains 39.4% of P_2O_5 and all the fluorapatite is presumably recovered from it?
2. Why does fine crushing of phosphorite increase the efficiency of phosphorite meal? Explain why the fertilizer should be added to soil during autumn ploughing (before sowing), and mixed with soil. Explain also the prolonged (during several years) action of phosphorite meal.
3. Determine the percentage of P_2O_5 in simple and double superphosphate (disregarding the presence of impurities).

3.5

Potassium Fertilizers

Potassium mineral deposits were not known in prerevolutionary Russia. The geological survey during the 1920s was a great success and the greatest deposit of sylvinite in the world was discovered near the town of Solikamsk. Thousands of millions of tons of this valuable mineral, which is actually crystals of potassium chloride intermixed with sodium chloride crystals, lie at the depth of 100–300 metres. Potassium salts are mined also in Byelorussia. The quantity of potassium salts quarried in the Soviet Union is measured by tens of millions of tons per year. Most of the potassium fertilizers used in the USSR is obtained from sylvinite.

How can potassium chloride be separated from sodium chloride? The solubility of sodium chloride almost does not change with decreasing temperature, while the solubility of potassium chloride decreases sharply. Therefore, when a solution of sylvinite that is saturated at 100°C is cooled to room temperature, most of the potassium chloride precipitates from the solution. The crystals are separated by filtration, while the solution is used to dissolve new portions of sylvinite. This is the industrial method of separating the chlorides of potassium and sodium, but it is rather complicated and expensive. Another method of separation is therefore widely used and is known as *flotation*. Sylvinite ore is crushed and placed in its saturated solution to which a reagent is added which sticks to the surface of potassium chloride but not to the surface of sodium chloride particles. As a result, the particles of potassium chloride (in contrast to those of sodium chloride) are not wetted by the water. When air is then passed through the mixture, the air bubbles stick to the surface of the potassium chloride grains. These float to the surface (hence the name of the method) and the potassium chloride is removed from the mixture together with foam.

Many green plants suffer from excess of the chloride ions. Among them are potatoes, grapes, and tobacco. One of the measures to remove the harmful effect of chlorine is to add chloride fertilizers in the autumn so that chloride ions could be washed out from soil. But a better way out is to use chlorine-free fertilizers instead of potassium chloride. These may be potassium phosphate or potassium nitrate. Potassium sulphate is obtained by special treatment of salts mined in the pre-Carpathian area.

High-quality potassium fertilizer is ash, which can be obtained locally by burning vegetable materials. In addition to potassium carbonate K_2CO_3, the ash also contains phosphorus compounds and microelements.

?

1. By what methods can potassium chloride be separated from sodium chloride in industry?
2. What products may be obtained by complex treatment of sylvinite?
3. Which potassium fertilizer contains the maximum percentage of K_2O? (Disregard the impurities.)

3.6 Manufacture of Mineral Fertilizers in the USSR

We can now understand how important fertilizers are to economy, and this chapter has shown the main problems associated with the manufacture of fertilizers and that have to be faced to raise the efficiency of agriculture.

The quantity of artificial fertilizers produced in pre-revolutionary Russia was very small, about 89 thousand tons. The output of fertilizers has increased significantly in the Soviet Union. In 1965 the chemical industry manufactured 31 million tons of fertilizers, in 1970 this figure increased to about 65 million tons and in 1980 to 95.3 million tons. The intensification of agriculture requires even greater quantities of fertilizers and with more attention being given to the manufacture of concentrated fertilizers.

Until recently mineral fertilizers were mostly used in the Soviet Union for soils used to grow technical crops (cotton, sugar beet, etc.). Since the output of fertilizers has risen significantly, they are now used for soils where food crops are grown (cereal, potatoes, vegetables, etc.). In order to increase the efficiency of fertilizers they must be used rationally.

The rapid advances in the chemical industry and chemization of agriculture require that secondary school students learn chemistry so that they can help solve the problems associated with the development of agriculture and the chemical industry.

4

Carbon Subgroup

4.1

Position of Elements of the Carbon Subgroup in the Periodic Table. The Structure of Their Atoms

The carbon subgroup is the main subgroup of the 4th group of the periodic table. The subgroup includes carbon, silicon, germanium, tin, and lead.

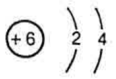
The outer electron layer of the atoms in the carbon subgroup contains four electrons: two paired *s* electrons and two unpaired *p* electrons. The outer layer thus contains the same number of electrons that it needs to be completed.

The most important elements of the 4th group of the periodic system are carbon C and silicon Si. The former is the most important element in all living organisms and the latter is the most abundant in the Earth's crust. Carbon and silicon are nonmetals. But they assume an intermediate position between the nonmetals whose atoms more easily accept electrons in reactions than donate them, and the metals that readily give off their valency electrons. One might therefore expect that the atoms of carbon and silicon will not give off or capture all electrons that they can donate or accept in reactions, but will form four covalent bonds. In the vast majority of their compounds, carbon and silicon are tetravalent.

4.2

Carbon

The chemical symbol of carbon is C, its atomic number 6, its atomic weight 12. The structure of the carbon atom is



Judging by the number of unpaired electrons, the carbon atom should be divalent. But the paired electrons contained in the carbon atom can disjoin and all four electrons become unpaired. The carbon atom is therefore tetravalent. The clouds of all four electrons are equally elongated while their axes are all directed toward the vertices of the tetrahedron (Fig. 4.1). The energy spent to disjoin the paired *s* electrons in the carbon atom is compensated by the energy evolved during formation of two new chemical bonds that arise between two distinguishing electrons and other atoms (carbon atoms included).

4.3 Allotropic Modifications of Carbon

Free carbon forms several allotropes. Diamond and graphite are among them. Both have atomic crystal lattice but the arrangement of atoms in them is different. We have already discussed the lattice of diamond. Each carbon atom in a diamond crystal is connected to four other atoms equidistantly located round it by covalent bonds (Fig. 4.1). All the bonds in diamond are equally strong.

Crystals of graphite are formed of atomic layers that can be likened to a pile of paper sheets. Each atomic layer is formed by interconnected six-membered rings of carbon atoms like a honeycomb (Fig. 4.2). The ability of carbon atoms to unite in such six-membered rings is as characteristic as formation of bonds between carbon atoms that are directed toward the vertices of tetrahedra. We shall get acquainted with carbon compounds containing six-membered rings in more details in the course of organic chemistry. The electron mechanism of formation of these compounds (the structure of graphite included) will then be explained.

Bonds between neighbouring layers of graphite are weak and a crystal can easily be separated into scales. Only three out of four valency electrons of each carbon atom in graphite are involved in the formation of ordinary covalent bonds. These three valency electrons form three bonds with the neighbouring atoms. The bonds are arranged at an angle of 120° to one another. The fourth electron remains free and movable like electrons in metals, hence graphite can conduct electricity. Owing to the different structures, diamond and graphite have quite different properties. Thus diamond is clear and colourless and does not conduct electricity; it is the hardest natural substance. Diamonds are used to cut glass, to drill rock, and in the manufacture of the cutting tools used in industry (cutters, drills, polishing discs, etc.) giving them high efficiencies and quality of operations (Fig. 4.1). Graphite is a grey opaque substance with a metallic lustre. The presence of moving electrons makes it a good conductor of electricity and heat; it is slippery (oily) to touch and is one of the softest solids known. On slightest friction against paper graphite layers separate and leave minute scales in the form of grey lines. Graphite is therefore used to make pencils. (The Greek word *graphein* means to write.) Owing to its softness, powdered graphite is used as a lubricant at high and also at very low temperatures. It packs the gap between an axle and the bush with its oily scales and thus decreases friction. Pressed graphite bushes are used in the manufacture of bearings. Owing to its electric conductivity, graphite is used in the manufacture of electrodes; it is also used to make heat-exchange tubes because of its heat conductivity (Fig. 4.2).

Free carbon occurs in nature in the form of graphite and separate crystals of diamond. Graphite is quite common but diamond occurs only very rarely. Natural diamonds occur in West Yakutia in the USSR.

The allotropic modifications of carbon are interconvertible at high temperatures. Diamond converts into graphite at high temperature and under normal pressure. Graphite can be converted into diamond at high

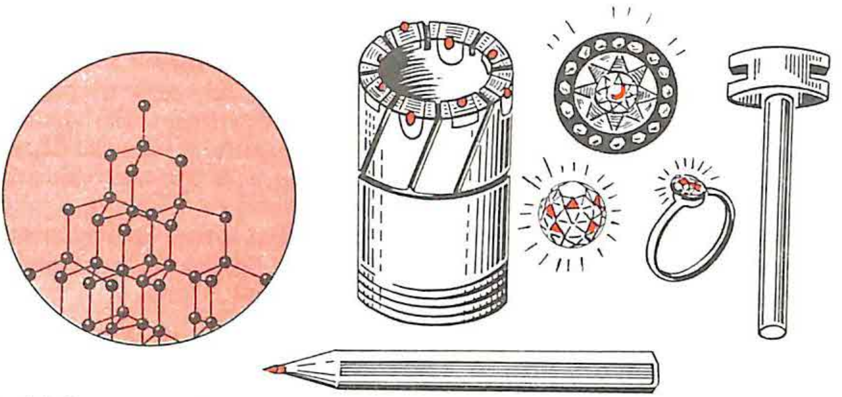


Fig. 4.1 Structure of diamond and diamond articles:

gem stones, rock drill bit, a glazier's diamond, a diamond pencil (diamonds are given in red)

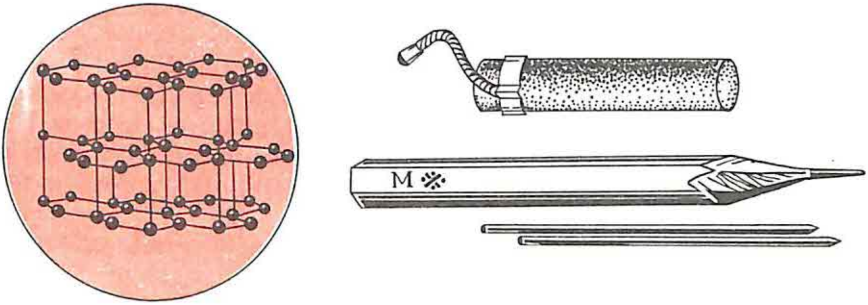


Fig. 4.2 Structure of graphite and graphite articles:

graphite lubricant, pencil, bushes, and electrode

temperatures and under very high pressures. Cutting tools made with artificial diamonds are not inferior to those made with natural diamonds.

In everyday life we often deal with other forms of carbon: carbon black (soot) and coal. These are amorphous allotropes of carbon similar to graphite except that they are divided into very fine particles. If paraffin lamp is not properly adjusted, soot is deposited on the glass. This is carbon black. Foods may burn in a frying pan and turn into a charred mass; this is also carbon. The same happens when we heat strongly a splint in a test tube without any air. The wood chars to turn into charcoal with evolution of combustible gases that may be ignited if we bring a burning match to the mouth of the test tube.

The thermal decomposition of organic substances in the absence of air (to prevent burning) *is called dry distillation or pyrolysis* (from the Greek *pyros* fire and *lysis* loosening or decomposition; compare 'hydrolysis').

Coal can be converted into coke by dry distillation.

The amorphous allotropes of carbon have various uses. Carbon black (soot) is used in the manufacture of the printing ink used to print the characters in this textbook. India ink is also made of soot. Carbon black added to rubber increases its strength and prolongs the service life of tyres and other rubber goods. The tyre industry is the main consumer of carbon black.

Coke is a fuel with a high calorific value and is used as a reductant in smelting out iron and other metals from their ores. Special grades of coal are used as adsorbing materials.

4.4. Adsorption

Free carbon is nonvolatile and nonmelting. Charcoal preserves the fine-porous structure of wood with its narrow channels through which sap moves in the living tree (Fig. 4.3). If the surface of all particles contained in powdered charcoal weighing 1 g, or rather the surface of all the pores and channels in a small piece of charcoal is summed up, the area would amount to many square metres.

Place pieces of charcoal (or powdered charcoal) into a flask filled with air containing nitrogen(IV) oxide: the brown colour of nitrogen(IV) oxide will vanish because nitrogen oxide will adsorb on the surface of charcoal. The charcoal itself will not change; it will only adsorb the nitrogen(IV) oxide in its pores like a sponge. Heat the charcoal: nitrogen(IV) oxide appears in the flask again. It has not changed either.

Add powdered charcoal to a litmus solution: the solution turns colourless because litmus has adsorbed on charcoal.

Adherence of gas or solute particles to charcoal or other solid is called adsorption. The higher the porosity of a given sample of charcoal, the greater the amount of gas or solute taken up. In order to increase the porosity of charcoal it is repeatedly heated in the absence of air and this process is called activating the charcoal. Residues of the products of the dry distillation that may clog the capillaries in the charcoal will thus be burned out.

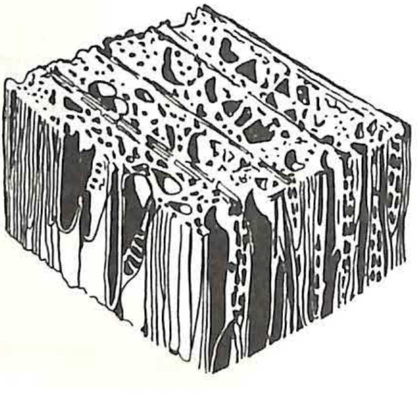


Fig. 4.3 Porous structure of wood remains in charcoal

Charcoal can adsorb all gases, noble gases included, but its adsorbing power differs for various gases. The easier a gas is liquefied, the stronger it is adsorbed by charcoal. The adsorbed gas can be recovered by heating the charcoal. This property is used for *regeneration* of charcoal, i.e. for restoration of its adsorbing power. Charcoal is used in the manufacture of sugar and alcohol to clean them from impurities. Activated carbon is available at pharmacy shops in the form of tablets and can be swallowed to remove noxious substances that may have accidentally entered the stomach. Active carbon is used in gas masks to protect the respiratory tract from noxious impurities in the air.

4.5 Chemical Properties of Carbon

Carbon stands in the periodic system almost in the middle between metals and nonmetals. It is therefore both electronegative, i.e. it acts as an oxidant in reactions with metals, and electropositive, i.e. acts as a reductant in reactions with nonmetals (oxygen included). The elements that are electronegative toward carbon are given in red in Table 4.1:

Table 4.1

III	IV	V	VI	VII	VIII
B	C	N	O	F	Ne
	Si	P	S	Cl	Ar

If carbon is heated to its ignition point, it burns in air, like in oxygen, without a flame or smoke to give carbon(IV) oxide:

$$C + O_2 = CO_2 + 402\ \text{kJ}$$

A flame is burning gas or vapour which is formed by substances that become volatile at the ignition point of a combustible substance. (Remember our earlier experiments in which we burned phosphorus, sulphur, or paraffin in oxygen.) Carbon is not volatile at the temperature at which it burns and it therefore burns without a flame; it only glows.

Carbon can take oxygen from other compounds. When heated, it reduces many metals from their oxides. When a mixture of two black powders, one is carbon and the other copper(II) oxide, is heated in a test tube it turns red: powdered copper metal is thus obtained, while the other reaction product is carbon(II) oxide:

$$C + 2CuO = 2Cu + CO_2$$

When an electric arc is formed between two carbon electrodes in a hydrogen atmosphere, carbon combines with hydrogen to form methane CH_4:

$$C + 2H_2 = CH_4$$

Methane is the main component of natural gas, which is used to heat and provide energy in many cities and plants. Many subterrain reservoirs of natural gas have been discovered in this country. Gas pipelines stretch over hundreds and thousands of kilometres to various towns and cities covering the country with a vast network.

Methane is not the only carbon compound with hydrogen. Remember the structure of diamond crystals: the carbon atoms can form strong covalent bonds not only with other elements but with carbon atoms too. If one of the four valency units of a carbon atom is spent to bond it to another carbon atom, three valency units remain in each of the two carbon atoms and they can attach six hydrogen atoms to form C_2H_6. If we thus continue the chain of carbon atoms, we get more complicated hydrocarbons: C_3H_8, C_4H_{10}, etc. Mixtures of hydrocarbons accumulate in nature in underground cavities in the form of petroleum and natural gas.

?
△

1. Describe the structure of (a) diamond and (b) graphite. Describe their physical properties with reference to the structures of their crystal lattices. What are practical uses of diamond and graphite?
2. Describe the known forms of amorphous carbon, the methods of their manufacture, and practical uses.
3. Describe adsoption and regeneration of activated charcoal, and practical uses of these processes.
4. Which gas is adsorbed better, ammonia or nitrogen? Explain.
5. Give formulas of compounds of carbon with (a) beryllium, (b) aluminium, (c) sulphur, and (d) fluorine. Superscribe the oxidation number of each element. Write the electropositive elements first.
6. Write the equations for the reactions between charcoal and the following oxides: (a) SnO_2, and (b) Pb_3O_4.
7. How much heat is liberated during burning of 1 kg of charcoal?

4.6

Carbon Monoxide

Carbon forms two oxides: CO and CO_2. Carbon(II) oxide CO, or simply carbon monoxide, is a colourless, odourless and tasteless gas. It is very poisonous. Only two out of the four valency electrons of the carbon atom are used to form electron pairs with the oxygen atom. The remaining two electrons can form two other covalent bonds by attaching another oxygen atom. This accounts for the following two properties of carbon monoxide: the combustibility and its reducing power (it can reduce metals from their oxides). Carbon monoxide burns with a blue flame to form carbon dioxide:

$$2C^{2+}O^{2-} + O_2^0 = 2C^{4+}O_2^{2-} + 572 \text{ kJ}$$

The colour of the flame can be seen at the lower margin of the flame of a burning candle or a match.

Carbon monoxide reduces most metals from their oxides. When carbon monoxide is passed through a heated tube containing copper(II) oxide, the black oxide is converted into red powdered copper:

$$Cu^{2+}O + C^{2+}O = Cu^0 + \overset{4+}{C}O_2$$

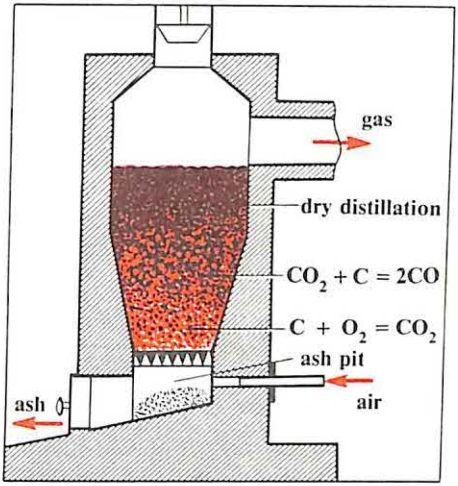


Fig. 4.4 Gas generator

Carbon monoxide does not react with water, alkalis or acids. Like nitrogen oxide NO it is a neutral (non-salt-forming) oxide.

Carbon monoxide is obtained by reacting carbon dioxide with very hot carbon

$$C + CO_2 \rightleftarrows 2CO - 160\ \text{kJ}$$

If we burn wood in a stove we can observe the formation of some carbon monoxide: blue flames flash over white-hot coals. This is the flame of carbon monoxide, which burns when air is admitted into the stove through the open shutter. When coals cool down, the blue flame dissappears: the reaction between carbon and carbon dioxide has stopped and the carbon monoxide is no longer produced.

We can now explain why a very hot coal burns with a blue flame and why this flame is absent if the coal is not very hot.

Carbon monoxide is contained in some gaseous fuels, in the producer gas in particular. A generator where this gas is obtained is loaded with a high bed of solid fuel, e. g. coke (Fig. 4.4), and air is supplied into it from below. The fuel burns in the lower portion of the bed and the carbon is converted into carbon dioxide:

$$C + O_2 = CO_2 + 402\ \text{kJ}$$

The carbon dioxide (together with the nitrogen from the air) passes through the bed of hot coke where it is reduced to carbon monoxide

$$CO_2 + C = 2CO - 160\ \text{kJ}$$

The resultant gas consists of carbon monoxide, nitrogen, and some other substances. This combustible mixture is called the producer gas.

If fuels other than coke (i. e. free carbon) are used in the gas generator, e. g. wood, the same reactions occur because wood turns into charcoal in the upper portion of the bed (pyrolysis). Volatile and combustible products of dry distillation are admixed to the producer gas.

The conversion of solid fuel into gaseous one is called gasification of fuels.

? △

1. Describe (a) the method of obtaining and (b) the properties of carbon(II) oxide. Give the reaction equations.
2. What is producer gas? Give the equation for the reaction by which it is obtained.
3. Describe the design and the operating principle of a gas generator.
4. The energy evolved during the formation of each mole of carbon dioxide from coal and oxygen is greater than the energy consumed for subsequent conversion of carbon dioxide into carbon monoxide. How do these energies relate?

4.7 Carbon Dioxide

Carbon(IV) oxide or CO_2 has the structural formula O=C=O and is a colourless gas. It is heavier than air and can be poured from one vessel to another like an invisible liquid. If we pour carbon dioxide from a beaker over alcohol burning in a dish (Fig. 4.5), the flame is immediately extinguished.

Carbon dioxide can be liquefied comparatively easily. When liquid carbon dioxide is evaporated, much heat is absorbed and part of liquid carbon dioxide solidifies into a white powder that looks like snow. Carbon dioxide is sparingly soluble in water, it does not burn, nor does it support the combustion.

Carbon dioxide has the properties of an acid oxide. When it is passed through a solution of lime water, the solution turns cloudy because calcium carbonate precipitates:

$$Ca^{2+} + 2OH^- + CO_2 = CaCO_3 \downarrow + H_2O$$

This reaction is so specific that lime water is used to detect carbon dioxide.

Millions of years ago the atmosphere of our planet consisted mainly of carbon dioxide. When plants appeared on Earth carbon dioxide was assimilated by them and oxygen evolved, which then began to replace the carbon dioxide in the atmosphere.

Carbon dioxide is formed in nature during the respiration of animals and the putrefaction of organic remains in soil. The air contained in soil therefore has less oxygen than atmospheric air has. It is heavier than air and therefore accumulates in dangerous concentrations in cellars and wells. The concentration of carbon dioxide is also higher in coal mines because the coal is slowly oxidized. The composition of the air in mines must therefore be tested constantly: the concentration of carbon dioxide in the air should not exceed 0.5 per cent by volume.

Carbon dioxide is the source of carbon for plants. The air in hot-houses is enriched with carbon dioxide to increase crop yields.

Carbon dioxide is used to gasify (carbonate) drinks. In the liquid state it is used in fire extinguishers. Pressed solid carbon dioxide is known as dry ice. The advantage of dry ice over common ice (frozen water) is that solid carbon

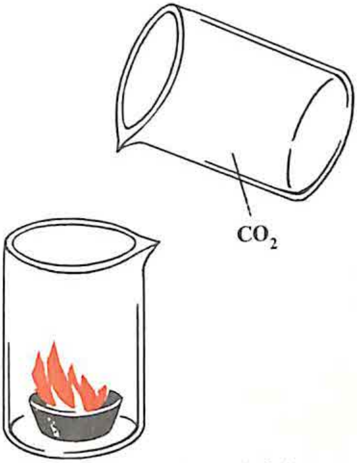


Fig. 4.5 Fire extinguishing with carbon dioxide

dioxide can produce much lower temperatures and that it 'melts' (evaporates) without giving water (i.e. omitting the liquid phase).

?
△

1. Describe (a) physical, (b) chemical properties of carbon dioxide, and (c) its uses in various states of aggregation, (d) method of detection, and (e) occurrence in nature.
2. Name the sources of carbon dioxide and how it is formed in nature, in the home, and in industry.
3*. Elements A and B react to give two compounds, C and D. The substance C is combustible while D is not, but it can be made combustible if it is combined with A. What are A, B, C and D? Write equations for these reactions and specify the conditions under which these reactions occur.

4.8 Carbonic Acid and Its Salts

When carbon dioxide dissolves in water carbonic acid H_2CO_3 is formed, which exists only at the moment it is formed and immediately falls into carbon dioxide and water:

$$H_2CO_3 = CO_2 + H_2O$$

Organic compounds in which two hydroxyl groups are bonded to the same carbon atom do not exist either. If such a compound were formed by any reaction then as in the case of carbonic acid, a molecule of water would also be eleminated from it and the double bond O=C=O would be formed.

Being dibasic, carbonic acid forms two series of salts, viz., acid and neutral. Neutral salts of carbonic acid are called carbonates (e.g. calcium carbonate, $CaCO_3$), while acid salts are bicarbonates (e.g. $Ca(HCO_3)_2$ or calcium bicarbonate). Carbonates of the alkali metals and ammonium carbonate are the only neutral salts of carbonic acid soluble in water.

Carbonates and bicarbonates are distinguished by their reactions with strong acids: the solution 'boils' to liberate carbon dioxide vigorously:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2CO_3 \begin{smallmatrix} \nearrow CO_2\uparrow \\ \searrow H_2O \end{smallmatrix}$$

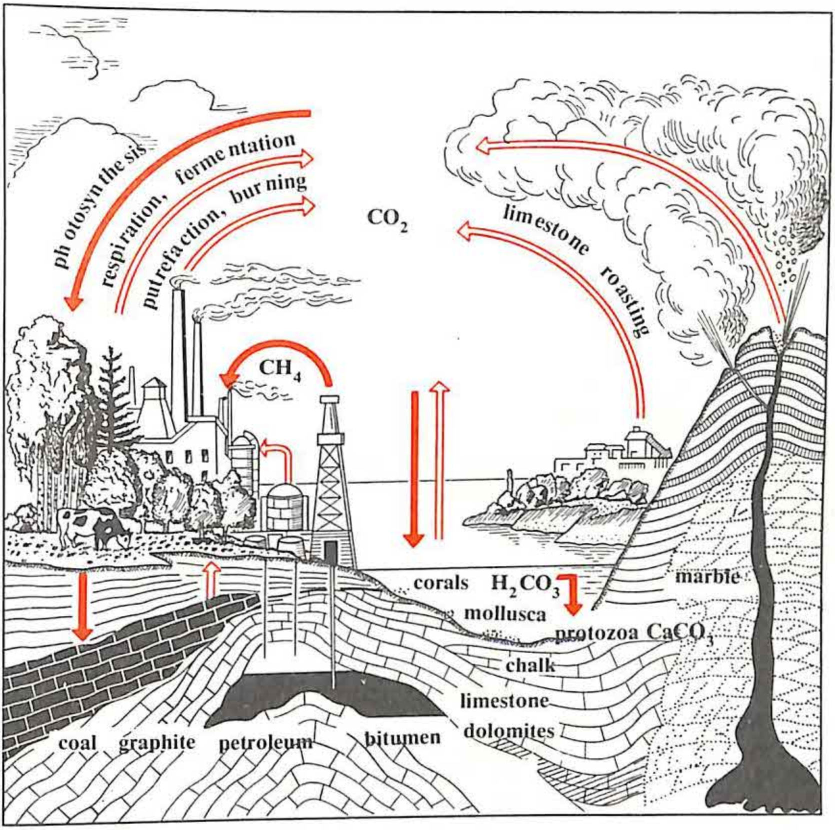


Fig. 4.6 Carbon cycle

dioxide, and follow its chemical conversions in nature. At the end of all conversions we shall have carbon dioxide again. Hence we can justly speak about carbon cycles in nature, the most important of them being the cycle in which living organisms are involved.

Photosynthesis, the main metabolic process of green plants, traps the carbon from atmospheric carbon dioxide incorporating it into plants, freeing oxygen into atmosphere. The process constantly replenishes the oxygen in the atmosphere and, as a consequence, the green plants grow. Animals feed on the plants and so their carbon passes into the animal body where it is turned into carbon dioxide again and returns to atmosphere (respiration). This cycle is interlaced with other carbon cycles.

Vegetable and animal remains are partly converted into combustible fuels: coal, petroleum, and natural gas. These are then extracted by man and used as fuel. When these fuels burn they liberate carbon dioxide, which is one of the products of combustion.

Both solid carbonates and their solutions can be tested by acids. The ionic equation of this reaction is

$$CO_3^{2-} + 2H^+ = CO_2\uparrow + H_2O$$

Since the hydrogen ions are bonded into a molecule during reactions of carbonates with acids, carbonates, like bases, can be used to neutralize acids. Limestone $CaCO_3$, for example, is crushed and added to soils to neutralize any excess acidity.

Owing to weakness of carbonic acid, aqueous solutions of carbonates are hydrolized and their solutions are strongly alkaline

$$CO_3^{2-} + H_2O \rightleftarrows HCO_3^- + OH^-$$

The most abundant carbonate is that of calcium. Its deposits occur rather frequently. One of the important objects of exploration in areas with acid soils is therefore to find deposits of calcium carbonate.

Sodium carbonate is an important salt manufactured artificially. This salt is known simply as soda and is used in the manufacture of glass, soaps, as a washing powder. When a soda solution is saturated with carbon dioxide it turns into sodium bicarbonate $NaHCO_3$. This salt is available at chemist's and food shops as 'baking soda'. It is taken to ease heartburn (pyrosis) which is caused by too much acid in the gastric juice.

Baking soda is used in making cakes and bread, in fire extinguishers as a source of carbon dioxide. When added to dough prepared without yeast it produces carbon dioxide bubbles in the dough (instead of the fermentation process) and these breads or cakes become porous, softer, more tasty and easier to assimilate.

△

1. Write (a) the electron and structural formula of carbonic acid, and (b) formulas of potassium and magnesium carbonates and bicarbonates. Name the salts.

2. Which of the following solutions will react with a solution of sodium carbonate: (a) sodium hydroxide, (b) calcium hydroxide, (c) sulphuric acid, (d) potassium nitrate, and (e) magnesium chloride. Write out the corresponding reaction equations.

3. Trapping carbon dioxide in lime kilns is done by passing the flue gas through a solution of potassium carbonate. When the solution becomes saturated with carbon dioxide, it is heated and the absorbed carbon dioxide is evolved. Write equations for the reactions that occur during this process.

4*. Invent a simple method by which concentration of calcium carbonate can be determined in a dried soil specimen containing no other carbonates. Not more than two weighings are allowed. Assume that the soil is free from water-soluble compounds and does not contain any insoluble phosphates.

4.9

Carbon Cycle in Nature

Like other elements, carbon atoms are not permanently contained in nature in the same compound but pass from one compound to another (Fig. 4.6). Take a carbon compound, e.g. carbon

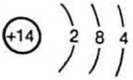
Carbon dioxide is also fixed during erosion of minerals and rocks, and returned to atmopshere by volcanos and mineral water springs.

The carbon cycle on the surface of the Earth is thus constantly active.

△ Follow up the main cycles of carbon on the surface of the earth.

4.10 Silicon

The chemical symbol of silicon is Si, its atomic number 14, and its atomic weight 28. The structure of its atom is



Silicon is only second to oxygen in its abundance on the earth. About 50 per cent of the mass of the Earth's crust is oxygen and almost 25 per cent is silicon. The Earth's crust mainly consists of compounds of silicon, oxygen, and other elements.

The outer layer of the silicon atom (like that of carbon) contains four electrons but they are located at a longer distance from the nucleus and so their attraction to the nucleus is weaker. Silicon's neighbours in the periodic system are the metals: aluminium to the left and germanium to the bottom. Therefore, although the nonmetallic properties prevail in silicon, it also has certain metallic properties.

Silicon crystallizes in the same crystal lattice as diamond. But unlike diamond, silicon conducts electricity when heated or when other elements are added. Silicon is semiconductor. The presence of electric conductivity in silicon makes it similar to metals. The appearance of silicon is also like that of metals (metallic lustre).

When heated strongly, powdered silicon burns to give silicon(IV) oxide SiO_2 known as silica

$$Si + O_2 = SiO_2 + Q$$

Compounds of silicon with hydrogen, e.g. SiH_4, are volatile but they are less stable than hydrocarbons. They ignite spontaneously on exposure to air and splash around bright sparks, which are actually white-hot particles of silicon(IV) oxide:

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O + Q$$

Silicon reacts with carbon to form silicon carbide, also known as carborundum SiC. Its crystal lattice is the same as in diamond and silicon but carbon and silicon atoms alternate: each silicon atom is connected with four carbon atoms, and vice versa. Carborundum is almost as hard as diamond, hence it is used as an abrasive material.

Free silicon is used in the manufacture of silicon steels which are characterized by their high refractoriness and acid resistance. Silicon is added to steels as an alloy with iron, ferrosilicon.

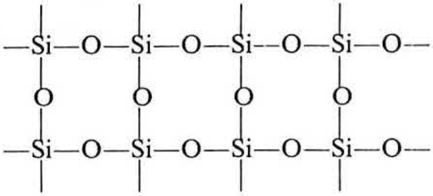
Artificially grown crystals of pure silicon are used as semiconductors in solar cells which convert the energy of the sun's radiation into electrical energy. Solar cells are indispensible in artificial satellites and space craft.

△

1. Describe the physical and chemical properties of silicon and its uses in the free state.
2. Draw the structural formula of carborundum, characterize its properties, and describe its practical uses.

4.11 Oxygen Compounds of Silicon

Silicon oxide SiO_2 is also known as silica. Unlike carbon dioxide, silica is a hard high-melting substance. The very different physical properties of CO_2 and SiO_2 are due to their different crystal lattices. Carbon dioxide crystallizes in a molecular lattice composed of loosely connected CO_2 molecules, while silicon dioxide has an atomic lattice, whose structure can be shown as:



This marked difference in the structure of these oxides is due to the different atomic radii of carbon and silicon. The carbon atom is so small that it can only hold two oxygen atoms by its side, bonding to each oxygen atom via two valency units thus forming the molecule $O{=}C{=}O$. The silicon atom can hold four oxygen atoms by each of its four valency units, while the other valency unit of each oxygen is spent to attach another silicon atoms. The atomic lattice is thus formed instead of molecular one. Each silicon atom thus becomes enclosed in a tetrahedron of four oxygens not only in silica but also in all the other oxygen compounds of silicon (silicic acids and their salts).

Silica occurs in nature as inclusions in granites and other rocks. These inclusions look like pieces of melted glass in the rock fragments. As the rock is destroyed by weather (erosion) these silica grains gather in beds of rivers in the form of white sand. Silicon dioxide occurs also in the form of beautiful single crystals whose size may be quite significant (see Fig. 4.7).

Crystalline silica is called quartz. Silica melts and solidifies slowly, which facilitates the manufacture of various articles from quartz (chemical glassware, for example). The thermal expansion of quartz is insignificant and quartz glassware can therefore be heated to high temperatures (to white hot)

Fig. 4.7 Natural crystal of quartz

and then dropped suddenly in cold water: it will not break or crack.

Silicon dioxide is an acid oxide. It does not react with water: rivers flow in their beds of silica for thousands of years and yet no product of water reaction with white sand has ever been discovered. The acid character of silicon dioxide shows itself when silica is melted with metal oxides, alkalis, or carbonates. Salts of silicic acid are then formed

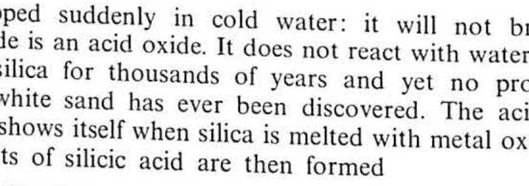
$$2NaOH + SiO_2 = Na_2SiO_3 + H_2O$$

Silicic acid can be obtained by acting on its salts with acids, e.g.,

$$2Na^+ + SiO_3^{2-} + 2H^+ + SO_4^{2-} = H_2SiO_3\downarrow + 2Na^+ + SO_4^{2-}$$

$$2H^+ + SiO_3^{2-} = H_2SiO_3\downarrow$$

It precipitates as a jelly-like substance to which the formula of H_2SiO_3 is conventionally assigned. But the precipitate is in fact a mixture of molecules interlaced into loose formations having approximately this structure



$$\begin{array}{c} \quad\;\; OH \quad\;\; OH \quad\;\; OH \quad\;\; OH \\ H{-}O{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}O{-}H \\ \quad\;\; OH \quad\;\; OH \quad\;\; OH \quad\;\; OH \end{array}$$

Each silicon atom appears to be inside a tetrahedron of four oxygen atoms. Like carbonic acid, silicic acid is an unstable compound which decomposes gradually into water and silicon dioxide

$$H_2SiO_3 = SiO_2 + H_2O$$

Silicic acid is very weak. Its salts are called silicates. Like carbonates, silicates of the alkali metals are only just soluble. Silicates of the alkali metals are known as soluble glass.

?
△

1. Describe the physical properties of silicon(IV) oxide. How do they differ from physical properties of carbon(IV) oxide? What uses of silicon dioxide do you know?
2. Describe the chemical properies of silicon(IV) oxide.
3. Describe the physical and chemical properties, and the method of preparing silicic acid. What is the difference between silicic and

carbonic acid, and what property is common to both of them?
4. Which salts of silicic acid are soluble in water and what are they called?
5. Some sand was dissolved by boiling it in a solution of substance x, which colours a flame yellow. Hydrochloric acid was added to the solution and a jelly-like substance was precipitated. Write equations for these reactions.
6*. How can silicic acid be prepared from silicon? Write down the reaction equations.
7*. Give a sequence of reactions for the conversion of a crystal quartz into porous silicon dioxide. The latter is known as silica gel.
8. Write the ionic equation for the hydrolysis of sodium silicate.

4.12 Colloidal Solutions

Silicic acid can form the so-called colloidal solution. When a substance is distributed in another substance, solutions or suspensions may be formed. Table salt mixes with water to form a clear solution, while chalk or clay forms a cloudy suspension in water. Solid particles suspended in a liquid form a *suspension*, while minute droplets of one liquid in another liquid form *emulsions*. Milk is an example of a typical emulsion (Fig. 4.8). Suspensions are unstable: depending on density, particles contained in a suspension gradually precipitate to the bottom or, vice versa, float to the surface of the liquid (cream is formed in milk this way).

The difference between suspensions and solutions is that a suspension is a *heterogeneous system*, while a solution is a *homogeneous one*. The degree of dispersion, i.e. the particle size, is also very important. In a solution the dispersion of a solute in a solvent is higher and the particle size is smaller than in a suspension or emulsion.

Colloidal solutions are intermediate between solutions and suspensions. A colloidal solution is a suspension containing particles whose size is so

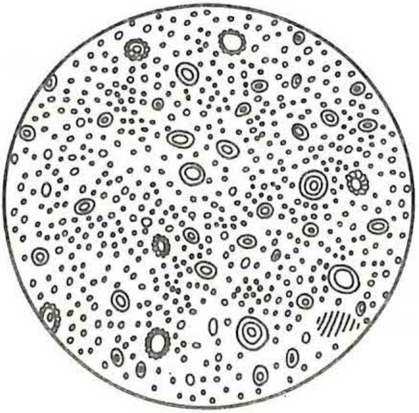


Fig. 4.8 Milk as viewed in a microscope

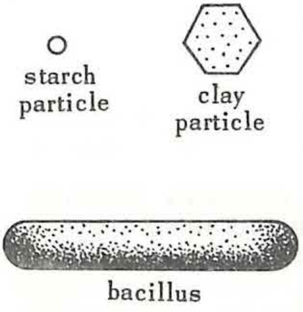


Fig. 4.9 Comparative dimensions of colloidal particles and a bacterium

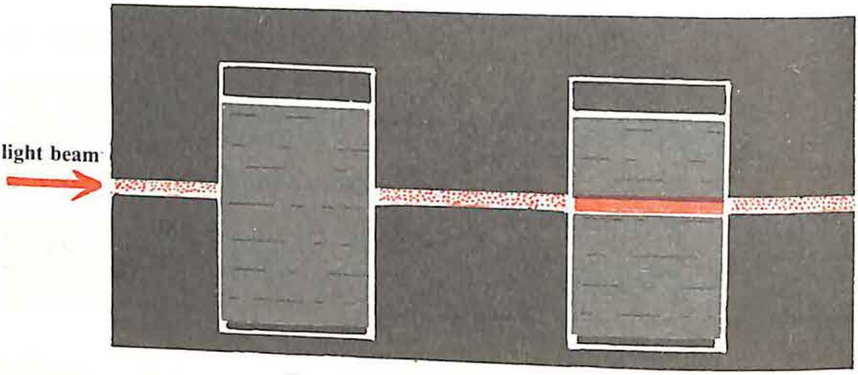


Fig. 4.10 A beam of light passing through: (*a*) a true solution and (*b*) colloidal solution

small (Fig. 4.9) that the liquid may be thought to be clear by an observer whereas the particles distributed in it are not single molecules but accumulations of them. Silicic acid H_2SiO_3 or ferric hydroxide $Fe(OH)_3$ are insoluble in water and true aqueous solutions cannot be obtained from these substances. Nevertheless clear liquids containing these substances can be prepared. These are colloidal solutions.

Add ferric chloride solution, drop by drop, into boiling water. Ferric chloride is a yellow substance while the clear liquid obtained is dark brown. This is a colloidal solution of ferric hydroxide which has formed due to the hydrolysis of the ferric chloride

$$FeCl_3 + 3HOH = Fe(OH)_3\downarrow + 3HCl$$

The net ionic equation is as follows:

$$Fe^{3+} + 3H_2O = Fe(OH)_3\downarrow + 3H^+$$

Egg white is also a colloidal solution. Glues, gelatin, or starch form colloidal solutions with water on heating, The word colloid is derived from the Greek *kolla* which means glue. The Greek suffix *-oid* means like or in the form of, and so *colloid* like glue.

How can a colloidal solution be distinguished from a true solution if both are clear? Suspended particles in a colloidal solution can be detected in the same way as dust particles can be detected in air. When a beam of light penetrates a slit in the shutter and passes into a dark room, it can be seen as a light 'path' (when viewed from the side). It is formed by dust particles that scatter the light. If we pass a lightbeam through a colloidal solution (e. g. ferric hydroxide solution) in a dark room, we can observe a similar sort of path because of the light being scattered by the colloid particles (Fig. 4.10). When a beam of light passes through a true solution (e. g. one of sugar or table salt), we do not observe any light path, even if the solution is coloured: molecules or ions contained in true solutions are too small to scatter light appreciably. However, there is no distinct difference between suspensions and colloidal solutions, or between colloidal solutions and true solutions. Substances are known, e. g. proteins, whose molecules are so large that they form colloidal solutions even though they exist as separate molecules in the liquid phase.

Colloidal particles do not precipitate no matter how long the solution may stand. They are in constant motion due to incessant collisions with the solvent molecules and this prevents their precipitation.

Why do colloidal particles not stick together even though they are constantly moving and colliding with one another?

The presence of an electric charge on colloidal particles prevents them sticking together. Different colloids have different charges. A colloidal particle becomes charged either through the elimination of an ion (anion or cation) from the particle's surface, which is what happens during the dissociation of electrolytes, or through the adsorption of anions or cations from solution onto the surface of colloidal particles. The hydrogen ion is, for example, eliminated from silicon hydroxide (as if it were an acid) into the solution and the particle becomes charged negatively. Particles of ferric hydroxide (since it is a base) eliminate the hydroxide ions from their surfaces and thus become positively charged. Since colloidal particles are similarly charged, they repell each other and cannot stick together to form larger aggregations. But if a solution of any electrolyte is added to a colloidal solution, for example if we add a few drops of ammonium sulphate $(NH_4)_2SO_4$ to a colloidal solution of ferric hydroxide, a brown substance, ferric hydroxide, is quickly precipitated. This happens because colloidal particles attract the oppositely charged SO_4^{2-} ions and are thus neutralized. They can now approach one another and stick together into larger particles, which precipitate.

The aggregation of colloidal particles into larger ones is called *coagulation*. The greater the charge of the adsorbing ions, the lower the concentration needed to induce coagulation.

Colloidal solutions often coagulate to form common precipitates, but in some cases the colloidal particles do not separate from the solvent and the entire colloidal solution turns into a semisolid mass known as a jelly, as is the case with the solidification of starch or gelatin solutions. Jellies are also formed during glues coagulation. When the water is evaporated, a glue becomes solid and can unite surfaces of various objects. When an egg is boiled, its white coagulates and the same thing happens with blood during its clotting.

We often observe coagulation in nature when river water containing various substances in the colloidal state meets with sea water which is rich in salts. Owing to coagulation of colloidal particles, silt is precipitated at the mouth of the river. Shallow waters are thus formed.

Colloidal solutions play an important role in nature and in industry. Soils are rich in colloidal solutions and phenomena that occur in them account for a soil's fertility. The protoplasm of all living cells and blood are colloidal solutions. Preparation of colloidal solutions, their coagulation and formation of jellies are all essential processes associated with the manufacture of glues, lacquers and varnishes, with textile dying, leather tanning, man-made fibres production, etc.

Colloidal solutions do not just form in water, sodium chloride can, for example, form a colloidal solution in benzene.

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1. What is (a) colloidal solution, (b) suspension, and (c) emulsion?
2. What are similar and different properties of (a) suspensions and colloidal solutions, (b) colloidal and true solution?
3. A solution of soap is colloidal and that of sugar, true. Prove it experimentally.
4. What is coagulation? What inhibits and what causes coagulation?
5. What happens if two colloidal solutions containing oppositely charged particles are mixed together?
6. In minor cuts during shaving we use the alum $KAl(SO_4)_2 \cdot 12H_2O$ to stop bleeding. Explain the reaction, if it is known that the colloidal particles of the blood albumins are charged negatively.
7. The least quantity of which of the following electrolytes will cause coagulation of (a) positively charged and (b) negatively charged colloidal particles: $Al(NO_3)_3$, Na_2SO_4, or $CaCl_2$?

4.13

Ceramics Industry

Silicon occurs in nature only in compounds with oxygen, viz. silicon dioxide (silica) and silicates. The latter often include aluminium, which is the third most abundant element on Earth after oxygen and silicon. Silicates containing aluminium are known as *aluminosilicates*. Their structure is complicated and is therefore normally expressed in terms of the oxides which combine to form the mineral. The composition of feldspar, for example, is expressed by the formula

$$K_2O \cdot Al_2O_3 \cdot 6SiO_2$$

The erosion of aluminosilicates by water and air gives compounds in which the alkali metal is replaced by hydrogen. For example, kaolinite has the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. This is the main component of clays. White (more frequently yellow) clays occur in nature. The colour of clays depends on admixtures of iron compounds.

Natural silica, silicates, and clay are raw materials used in the ceramics industry for manufacture of ceramics, glass, and cements.

Ceramics. The word originates from the Greek *keramikos* meaning earthenware. The main raw material for the manufacture of ceramics is clay. Clays consist of very small crystals (Fig. 4.11), having the shape of platelets. Owing to this configuration, clay platelets come in close contact without forming any gaps of voids. Therefore, unlike sand clays do not allow water through. If water is added to a clay and mixed thoroughly, an elastic mass is formed that can be shaped into different articles. After drying and firing such an article becomes a hard *ceramic*. Ceramic construction materials have been known from times immemorial and they are still being improved. Ceramics

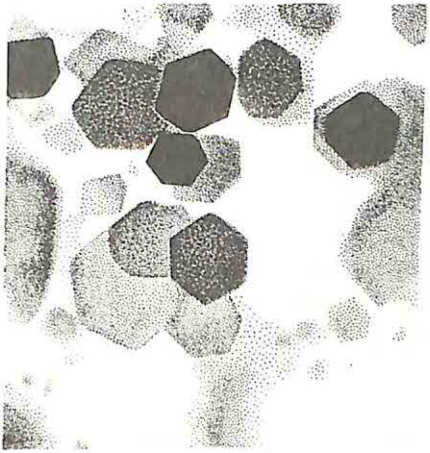


Fig. 4.11 Clay crystal (× 15 000)

are used in industry, in the home, and in the arts. White clays are used to manufacture porcelain, pottery, and earthenware. An article shaped from clay is hardened at a high temperature and allowed to begin sintering, after which the heating is discontinued to prevent clay from melting. Ceramic articles are therefore porous and allow moisture through them. In order to remove this disadvantage the articles are glazed with special substances which melt at moderate temperatures to form thin glass-like coatings on the ceramic's surface.

Glass. Glass is normally made from white sand, lime, and soda by sintering their mixture. Limestone and soda are decomposed to liberate carbon dioxide, while the formed metal oxides (sodium and calcium oxides) combine with silicon dioxide to turn into silicates

$$Na_2O + SiO_2 = Na_2SiO_3$$

$$CaO + SiO_2 = CaSiO_3$$

The silicon dioxide is taken in excess quantities and so the manufactured glass is a cooled melt of sodium silicate, calcium silicate and silica. An approximate formula of normal glass is $Na_2CaSi_6O_{14}$, or it can be given as a compound consisting of oxides: $Na_2O \cdot CaO \cdot 6SiO_2$. The main property of glass is that it passes from a liquid to solid state slowly as the temperature falls until it solidifies completely, and not in an abrupt jump. Glassblowing, rolling glass into sheets, and drawing glass fibres depend on this property of glass. Portions of liquid glass are taken from a bath and the articles are blown or pressed into different shapes. Special machines are used to draw sheet glass (Fig. 4.12) and glass tubes.

The properties of glass can be varied arbitrarily within wide limits by replacing the basic oxides of sodium and calcium by oxides of other univalent and divalent metals, and by substituting boron(IV) oxide for the acid oxide of silicon(IV). If, for example, potash (potassium carbonate) is substituted for soda (sodium carbonate), a more refractory glass is obtained which is used for the manufacture of laboratory glassware. If lead oxide is also substituted for calcium oxide, flint glass, or crystal, is obtained. This type of glass refracts light very strongly and is used to make lenses and prisms, and also pieces of art. Coloured glasses are prepared by adding metallic compounds whose ions have the required colour to the initial mixture.

Cement. This is the most important modern construction material. It is prepared by burning crushed limestone and clay in rotary kilns where the components are sintered. The kilns are installed in the inclined position and rotate slowly. The starting materials are loaded at the upper end of the kiln and move slowly down towards its lower (discharge) end to meet a countercurrent flow of hot gas which is produced by burning a liquid fuel. The limestone liberates carbon dioxide and the clay gives off its water. The remaining oxides of calcium, aluminium, and of silicon form calcium silicates and calcium aluminates which make up the cement. The formed clinker pellets of cement are then ground to a powder and packed in water-proof bags. When the cement is mixed with water, a gradually setting mixture is obtained.

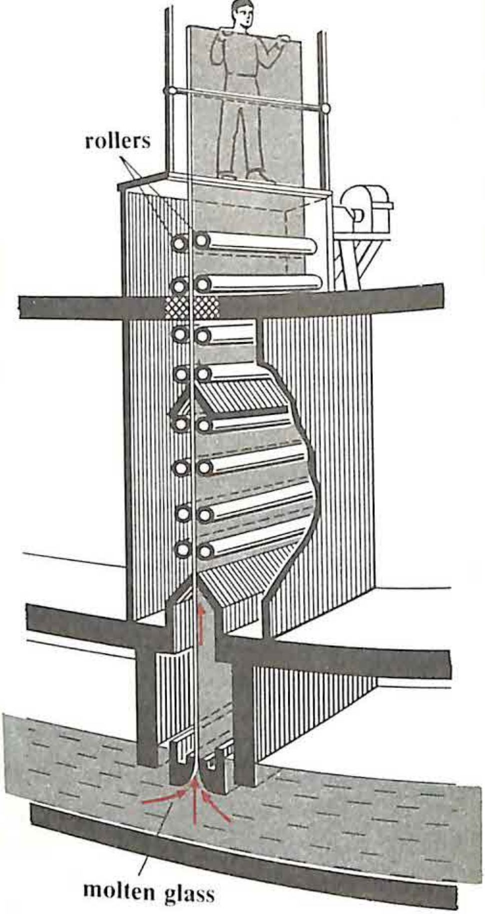


Fig. 4.12 Drawing glass sheets

In order to increase the volume of the setting mixture, sand or crushed stone or gravel are added to cement before mixing with water. This mixture is known as *concrete*. The strength of concrete structures is greatly increased if frameworks of wires or iron rods are placed inside the bulk of the concrete mixture. This is called *reinforced concrete*, and is widely used in construction of houses, dams, etc.

A vast amount of construction is carried out in the Soviet Union, and the Communist Party does its best to hasten the growth and improvement of the building industry and the building materials industry. The main construction materials that are required are cement, concrete, and reinforced concrete.

?
△

1. What is the ceramics industry, what raw materials are used in it and what are its main products?
2. Which of the properties of clay are utilized in the manufacture of ceramic articles?
3. Which properties of cement account for its main uses?
4. Briefly describe the manufacture of (a) glass, and (b) cement.
5. What is (a) concrete, and (b) reinforced concrete?
6. Write equations for the reactions occurring during the manufacture of glass if the starting materials are potash K_2CO_3, lead oxide PbO, and white sand.
7. Silica bricks are produced in the Soviet Union on a large scale (second only to clay bricks). Silica bricks are made of white sand and slaked lime. They are actually grains of quarts bonded by calcium silicate. Write the equation for the reaction by which silica brick is prepared.

■ Calcine dry clay in a test tube. Observe the reaction and write its equation. This reaction occurs when ceramics are fired.

4.14 General Characteristics of Elements in the Main Subgroup of Group IV

The atomic radii increase with the atomic numbers of elements in the subgroup (carbon, silicon, germanium, tin, and lead), and the attraction of the outer electrons to the nucleus weakens, thus increasing the metallic character of the elements in the free state. Germanium looks more like metal than silicon but is brittle. Like silicon, germanium is a semiconductor, i.e. assumes an intermediate position between insulators and conductors (metals). Germanium crystallizes in the same lattice as diamond and silicon. Having semiconductor properties, germanium crystals are used in electronics.

Tin and lead both have metallic properties, such as metallic lustre, high electrical and heat conductivity, and ductility. The appearance of tin is well known from everyday experience (tins, tin-plated iron, etc.). The appearance of lead is also known to us: the weights used in fishing, cable covering, and storage batteries are all made of lead. The specific metallic properties account for all the uses of these two metals.

Another result of increasing atomic radii in the elements of this subgroup is their decreased electronegativity which shows up in decreased strength of chemical bonds with electropositive (toward them) elements, e.g. with hydrogen.

■ Write a short report on the practical use of semiconductors.

4.15 Comparison of Hydrogen Compounds of Nonmetals in Various Subgroups

When we studied nonmetals, we devoted special attention to their hydrogen compounds which are especially characteristic of them. Let us remember what hydrogen compounds may be formed by chemical elements. The hydrogen atom can accept electrons ($H + \bar{e} = H^{1-}$) and donate them ($H - \bar{e} = H^{1+}$). Compounds in which hydrogen is electronegative and is contained as the hydride ion H^-, are nonvolatile and have high melting points, like all ionic compounds. These compounds are called *hydrides.* Hydrides are formed by elements with pronounced metallic properties, e.g. Na^+H^-, $Ca^{2+}H_2^{1-}$. In the molten state hydrides dissociate into the metal ions and the hydride ions H^-.

Hydrogen is electropositive in compounds with most typical nonmetals. The compounds formed by nonmetals with hydrogen, such as, $H_2^{1+}O^{2-}$, $H^{1+}Cl^{1-}$, or $H_2^{1+}S^{2-}$ have a molecular lattice. They are therefore low-melting and volatile. In ordinary conditions these compounds are gases or volatile liquids (water). Covalent polar bonds are found in these hydrogen compounds.

Let us now compare the properties of hydrogen compounds of elements in various subgroups of the periodic system.

The different properties of hydrogen compounds of nonmetals are especially marked when they dissolve in water. Group VI and VII hydrogen compounds dissociate in aqueous solutions into the hydrogen ion and the anion of the corresponding nonmetal:

$$HBr = H^+ + Br^-$$

$$H_2Te = 2H^+ + Te^{2-}$$

They thus dissolve in water to form acids (see Table 4.2).

The hydrogen compound of oxygen is characterized by properties that are very specific compared with hydrogen compounds of other nonmetals of the VIth and VIIth groups. This compound is water. Water dissociates into hydrogen ions and hydroxide ions and therefore has dual (amphoteric) properties.

Let us now discuss hydrogen compounds of the group V elements. Ammonia NH_3 and phosphine PH_3 show basic properties in their aqueous solutions. This can be explained by that their molecules attach hydrogen ions present in the solution by the donor-acceptor mechanism (see page 42) and the hydroxide ions are thus left in excess.

Hydrogen compounds of nonmetals of group IV, methane and silane, are sparingly soluble in water and display neither basic nor acid properties in their aqueous solutions. Hydrogen ions do not separate from their molecules in water because the hydrogen is too tightly bonded to the nonmetal atom. At the same time these compounds do not attach hydrogen ions from the water because neither methane nor silane molecules have any free electron pairs that are not involved in the formation of chemical bonds.

The strength of acids and bases formed by the hydrogen compounds of

Table 4.2

Period	Group					
	IV	V	VI		VII	
II	$C^{4-}H_4^{1+}$	$N^{3-}H_3^{1+}$	$H_2^{1+}O^{2-}$		$H^{1+}F^{1-}$	
		∨				
III	$Si^{4-}H_4^{1+}$	$P^{3-}H_3^{1+}$ bases	$H_2^{1+}S^{2-}$	<	$H^{1+}Cl^{1-}$	nonmetal atom radius increases
			∧			
IV			$H_2^{1+}Se^{2-}$	<	$H^{1+}Br^{1-}$	strong acids ↓
V			$H_2^{1+}Te^{2-}$	<	$H^{1+}I^{1-}$	

acids

←

Oxidation state of nonmetals decreases

The > sign indicates that the compound is stronger than that at which it points with respect to its acid or basic properties

nonmetals (Table 4.2) changes regularly in subgroups of the periodic system. The strength of acids increases from top to bottom and from left to right. How can this be explained?

The attraction between oppositely charged particles diminishes with decreasing charge and increasing distance between them; this is why hydriodic and hydrobromic acids are the strongest among acids formed by nonmetal hydrides.

Uninegative ions I^- and Br^- have larger radii than the other nonmetal anions, and so do not form strong bonds with hydrogen ions in aqueous solutions. Hydriodic and hydrobromic acids are almost fully dissociated in aqueous solutions.

Doubly charged nonmetal ions, or singly charged ions with radii smaller than I^- or Br^- ions, form stronger bonds with hydrogen ions. The degree of dissociation in the corresponding binary acids will therefore be lower than in hydriodic and hydrobromic acid.

Let us explain now why the hydrogen compound of nitrogen NH_3 has stronger basic properties than the hydrogen compound of phosphorus PH_3. Both substances dissolve in water to attach hydrogen ions and thus create excess hydroxide ions. Owing to the higher positive charge of the phosphorus nucleus (compared to the charge of the nucleus of the nitrogen atom) the ability of phosphine to attach the positive hydrogen ion is weaker than in ammonia.

?
△

1. Compounds of hydrogen with metals are nonvolatile, and with nonmetals, volatile. Why?
2. Hydrogen evolves in reactions between metal hydrides and water, for example: $LiH + H_2O \rightarrow LiOH + H_2\uparrow$. Write the ionic equation for this reaction and explain it as an oxidation-reduction reaction.
3. How does the strength of binary acids depend on (a) the charge of the anion and (b) its radius? Which of them are strong? Which is the strongest?
4. Test tubes contain equal volumes of sodium sulphide and sodium selenide solutions of the same concentration (in mole/litre). In which solution the concentration of the hydroxide ions is higher? (First write equations for hydrolysis of the salts.)
5. Unlike ammonia, phosphine PH_3 reacts only with strongest acids. Explain.
6. Use the symbol Nm to designate nonmetals and write general formulas of hydrides of nonmetals of (a) VIIth group, (b) VIth group, (c) Vth group, and (d) IVth group of the periodic system. Nonmetals of which group exhibit (a) the highest and (b) the lowest oxidation number?
7. What properties are common to hydrogen compounds of (a) nitrogen and phosphorus, the nonmetals of group V, (b) carbon and silicon, the nonmetals of group IV?
8. Which hydrogen compounds of nonmetals have most pronounced acid properties in aqueous solutions? Which of them have most pronounced basic properties? Give equations for the reactions of these compounds with water.

5 General Properties of Metals

Man cannot live without machines now. Some of them perform simple mechanical operations and substitute for the weak muscles of man, others do very precise jobs that man can never do himself. Electronic machines (computers) substitute in many cases for the human brain. The greater the number of machines that are produced and usefully applied, the faster industry, transport, and agriculture develop and the higher the efficiency of labour. But all machines are made of metal.

Most chemical elements are metals and are contained in all groups of the periodic table. The first three groups consist solely of metals, except for hydrogen in the first and boron in the third group. Metals are contained not only in the secondary subgroup but also in the main subgroups of groups IV, V, VI, and VII. All chemical elements in the secondary subgroup of group VIII are metals.

It should, however, be remembered that many chemical elements, which would normally be referred to as metals, also have nonmetallic properties. However, the latter are not so pronounced as metallic properties.

We have already had a general acquaintance with metals. Now we shall discuss them in more detail.

5.1 Structure of Metals

Particles in metals in the liquid and solid state are connected together by chemical bonds that are not yet known to us. In order to explain how these bonds arise, remember that typical metals are characterized by a small number of electrons in the outer layer of their atoms, and relatively low energy is required to ionize them.

During condensation of metal vapour the atoms approach one another, and their outer electrons become shared by all atoms in a given piece of metal. Positive ions of the metal (cations) are held together by their bonds with all freely moving electrons in the metal. This is called *metallic bonding* (Fig. 5.1).

The metallic bond in certain respects resembles a covalent and an ionic bond, but it also differs from both of them. The similarity to covalent bonding is that it is also associated with the sharing of valency electrons between atoms. But in metallic bonds, valency electrons bond together all atoms in a given piece of metal, while in covalent bonds they are shared by only two atoms that are thus united.

The presence of ions accounts for similarity of metallic and ionic bonds. But positive ions in metals are held by freely moving electrons while in

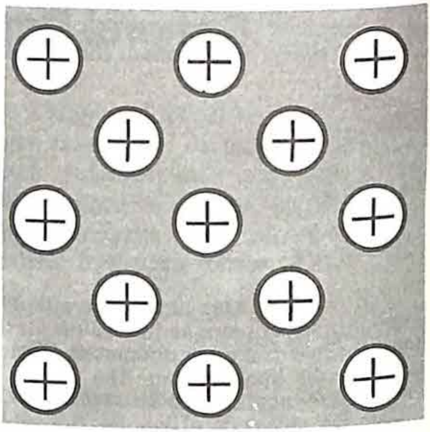


Fig. 5.1 Schematic diagram of a metal crystal

substances with ionic bonds these ions are attracted to negative ions.

Metallic bonding occurs in solid and liquid metals. Solid metals are crystalline substances. Their crystal lattices are similar to atomic lattices except that only positively charged ions are located at the points of metal lattices.

All freely moving electrons are attracted by the cations and the metallic bond is therefore very strong. Crystal lattices (Fig. 5.2) with close ion packing are therefore characteristic of metals. Close packing is attained in metals with *hexagonal lattices* (zinc, magnesium, chromium, etc.) or *face-centred cubic lattices* (copper, silver, aluminium, etc.). A *body-centred cubic lattice* is less packed. Iron, sodium, barium, for example, have this type of crystal lattice.

Some metals can crystallize and, depending on the temperature, can form several different lattices. Tin, for example, forms a crystal lattice similar to that of diamond below 13°C, but if tin is crystallized above 13°C, its lattice is body-centred cubic. Gray tin (the α modification) is formed below 13°C, and white tin (the β modification) above 13°C. The formation of various modifications of iron will be discussed later.

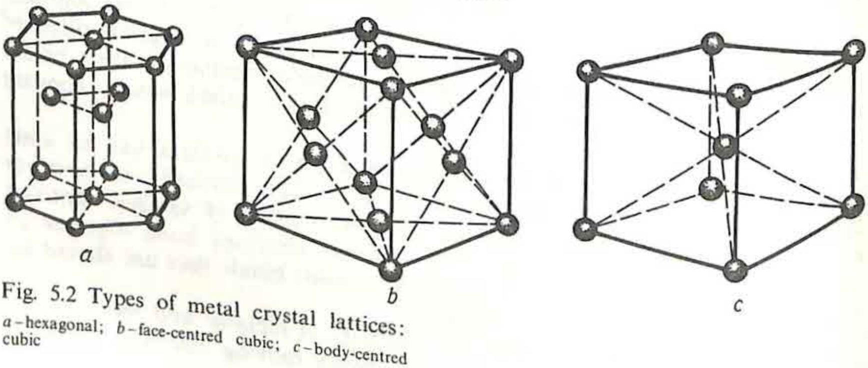


Fig. 5.2 Types of metal crystal lattices:
a – hexagonal; *b* – face-centred cubic; *c* – body-centred cubic

?

△

1. Describe the structure of metals and the nature of metallic bonding.
2. If a metallic rod moving at a high speed is stopped suddenly, a negative charge arises for a short time at its leading end and a positive charge at the trailing end. Explain the phenomenon.

5.2

Physical Properties of Metals

The inner structure of metals accounts for their characteristic physical properties.

1. *Ductility*. When a piece of metal is deformed (its shape altered mechanically), ion layers are displaced relative to one another. A fracture does not occur because the bonding electrons have also been displaced accordingly and continue bonding the displaced ions.

2. *Electrical conductivity* occurs because of free movement of the electrons about the entire piece of metal since none of them belong to any particular atom.

3. High *heat conductivity*. The same electrons mainly account for the transfer of heat from one part of metal to another. Electrons account for the specific optical properties of metals, viz., *metallic lustre* and *opacity to light*.

We can identify metals and their alloys by their lustre. Metals shine because they reflect light from their surfaces instead of absorbing it like soot (carbon) or letting it pass through them like glass.

These described properties are manifested in different ways in various metals. The metallic lustre, for example, is very characteristic of silver (hence its use in the manufacture of mirrors). When we look in a mirror we can see our image reflected from the thin coat of silver applied to the back surface of the glass.

Silver is the first among other metals with respect to its electrical conductivity. Next follow copper and aluminium. But silver is expensive and copper and aluminium are therefore used to make electric wires. Electricity is conveyed over hundreds of kilometres from power stations where it is generated. The distribution of electricity is done via copper and aluminium wires.

The electrical conductivity of other metals varies within very wide limits. The conductivity of tungsten, for example, is 340 times worse than that of silver. Industry also needs metals with moderate electrical conductivities and they are used in the manufacture of electric heaters.

The filament of an electric bulb becomes hot because of its resistance to an electric current passing through it. The metal used to make filaments should therefore have a low electric conductivity. Tungsten is now mainly used for the purpose.

The heat conductivity of metals is proportional to their electrical conductivity. All metals are therefore arranged by their heat conductivity in the same series in which their electrical conductivity decreases: silver, copper, aluminium, etc.

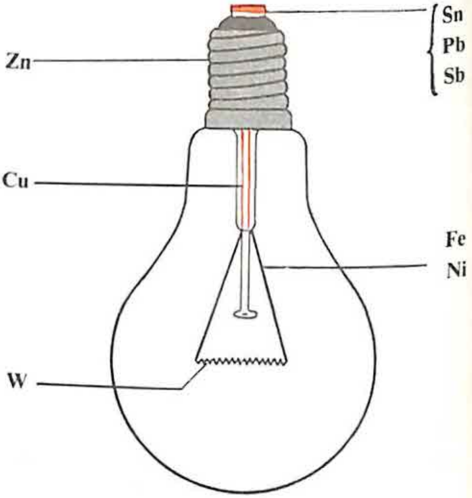


Fig. 5.3 Eight metals are used in the manufacture of an electric bulb

Ductility is the specific property of metals: they are not broken into pieces when we strike them with a hammer. Metals are malleable, i.e. they can be forged into different shapes. Gold is the most ductile metal. It can be rolled into very thin sheets that are semipervious to light, or can be drawn into a very thin filament that is invisible to the naked eye.

The melting point, density, and hardness are other physical characteristics that are very important for practical uses of metals. Densities of metals are directly proportional to their atomic weights. The smaller the atomic weight and the greater the atomic radius of the metal, the smaller is its density. Why? Densities of metals vary within very wide range, from 0.5 g/cm^3 in lithium to 22 g/cm^3 in osmium. Metals whose specific gravity is below 5 g/cm^3 are called light metals. Magnesium, aluminium, and titanium are light metals used in construction. They are mainly used to make transportation equipment: titanium is used for building of supersonic aircraft. Air friction at supersonic speeds is so high that the metal sheets become very hot. The strength of a metal is, however, known to decrease with increasing temperature and at its melting point becomes zero. Titanium is characterized by a high melting point and its strength (in contrast to aluminium alloys) does not decrease at temperatures it is heated to in supersonic flights.

When, in rare cases, the density of a metal is of primary importance (shot, bullets), lead is used, although its density is about two times lower than that of the heavies metals, which are, however, very expensive.

The melting point and hardness of metals depend mainly on the strength of metallic bond. It differs in various metals and is especially strong in heavy metals whose penultimate layers are filled with electrons. These metals are high-melting and hard.

Melting points of metals vary within wide limits as well: from −39°C for mercury to 3 410°C for tungsten. Mercury is the only metal which is liquid under normal conditions and is therefore used in measuring instruments. Tungsten is used whenever high temperatures have to be withstood, for example in filaments of electric bulbs (Fig. 5.3).

The hardness of metals differs as well. The alkali metals are soft as wax, while the hardest metals, e. g. tungsten and chromium cannot be worked by hardened files.

?

1. What are the general physical properties of metals? Explain them from the standpoint of the theory of metal structure. Name metals in which a given property is most pronounced and give examples of practical uses of these metals which depend on this property.

△

2. Which is the lightest and which is the heaviest metal? Which metal has the lowest melting point and which the highest? Which metals are the softest and which the hardest?
3. Give examples of uses of (a) tungsten, (b) mercury, (c) copper, and (d) silver in household articles. What physical property of each metal accounts for its use?

5.3

Chemical Properties of Metals

The atomic structure of metals accounts not only for their physical properties but for their chemical properties as well. However varied the chemical reactions of metals may be, they all are oxidation-reduction reactions of two types: addition and substitution reactions. In all chemical reactions metals give off their electrons, i. e. act as reductants and exhibit only positive oxidation numbers.

In the general form this can be expressed as:

$$\mathrm{Me}^0 - n\bar{e} \rightarrow \mathrm{Me}^{n+}$$

where Me^0 is a metal as a simple substance and Me^{n+} is the metal in a chemical compound.

One might suppose that metals can give off their valency electrons to the atoms of nonmetals, hydrogen ions, ions of other metals, and will therefore react with nonmetals (simple substances), water, acids, and salts. But the reducing power differs in metals. Moreover, the oxidizing power of the substances with which metals react differs as well, hence the conditions under which a particular reaction occurs are therefore very important. Whether or not a given metal will react with a particular oxidant, and what products will be formed during this reaction, will depend on the reaction conditions. Most metals burn in oxygen at high temperatures:

$$2\overbrace{\mathrm{Mg}^0 + \mathrm{O}_2^0}^{4\bar{e}} = 2\mathrm{Mg}^{2+}\mathrm{O}^{2-}$$

However, silver, gold, platinum and some other metals are not oxidized in these conditions.

Most metals react very actively with the halogens. Aluminium, for example, burns in bromine at room temperature:

$$2\overbrace{\mathrm{Al}^0 + 3\mathrm{Br}_2^0}^{6\bar{e}} = 2\mathrm{Al}^{3+}\mathrm{Br}_3^{1-}$$

All metals, except gold, combine with sulphur. Active metals react with sulphur with explosion. A copper wire becomes hot in sulphur vapour:

$$\overbrace{\mathrm{Cu}^0+\mathrm{S}^0}^{2\bar{e}}=\mathrm{Cu}^{2+}\mathrm{S}^{2-}$$

Some metals react with water to give the corresponding hydroxides. The alkali and alkaline earth metals react very actively with water under normal conditions. The general diagram of this reaction is as follows:

$$\mathrm{Me}^0 + \mathrm{HOH} \rightarrow \mathrm{Me}^{n+}(\mathrm{OH})_n + \mathrm{H}_2\uparrow$$

Other metals react with water at higher temperatures. Magnesium reacts with boiling water, and red-hot iron with steam. Metal oxides are obtained in these reactions.

If a metal reacts with an acid, it becomes a part of the salt obtained. When a metal reacts with a binary acid, it is oxidized by the hydrogen ions which are present in this solution. The net ionic equation of such a reaction is as follows:

$$\mathrm{Me}^0 + n\mathrm{H}^+ \rightarrow \mathrm{Me}^{n+} + \mathrm{H}_2\uparrow$$

Anions of oxyacids (concentrated sulphuric and nitric acids) are stronger oxidizers than the hydrogen ions. Some metals, for example copper and silver, which cannot be oxidized by hydrogen ions, react with sulphuric and nitric acids.

Below we shall establish which metals can react with solutions of acids or salts.

?
△

1. Characterize the general chemical properties of metals.
2. Describe schematically a reaction between a metal and a nonmetal. Use the symbol Me for metal, Nm for nonmetal, and designate the oxidation state of the metal as $n+$, and that of the nonmetal, $m-$.
3. Write equations for reactions between (a) aluminium and sulphur, (b) barium and water, (c) zinc and hydrochloric acid, and (d) copper and concentrated sulphuric acid. Indicate substances that act as oxidants and reductants in the reactions.
4. Give examples in which metals are involved in reactions of (a) addition and (b) substitution. Explain the role of metals in these reactions.

5.4

Electrochemical Series

If a piece of copper (a coin or a wire) is placed in a solution of any salt of iron, e.g. its sulphate $\mathrm{FeSO_4}$, no reaction occurs: copper does not displace iron from its salt. However, place a piece of iron (a nail) into a solution of a copper salt, e.g. $\mathrm{CuSO_4}$: copper will be readily deposited as a red metal on the iron, while the blue colour of solution, which is characteristic of the hydrated copper ions, will vanish gradually to turn into green, which is characteristic of the hydrated iron ions. Iron thus displaces copper from its solutions:

$$\overbrace{\mathrm{Cu}^{2+}+\mathrm{Fe}^0}^{2\bar{e}}=\mathrm{Cu}^0+\mathrm{Fe}^{2+}+Q$$

The reaction consists in the transfer of electrons from the iron atoms to the copper ions. Iron displaces copper because its atoms give off its electrons more readily than the copper atoms. The easier the metal atom gives off its electrons, the more active the metal. Iron is more active chemically than copper.

If a drop of mercury is placed in a copper(II) sulphate solution, no reaction occurs: mercury does not displace copper from solutions of its salts. If, on the contrary, a piece of copper (e.g. a copper plate) is placed in a solution of a mercury salt, e.g. $Hg(NO_3)_2$, the copper plate will immediately become coated with mercury (which will look like silver). Metallic mercury will be deposited on the copper surface. The solution, that was formerly colourless, turns blue, the colour being characteristic of the hydrated copper(II) ions. Copper displaces mercury from its salts:

$$\overbrace{Hg^{2+} + Cu^0}^{\xleftarrow{2\bar{e}}} = Cu^{2+} + Hg^0 + Q$$

The reaction consists in transition of the electrons from the copper atoms to the mercury ions. Being less chemically active than iron, copper is more active than mercury.

The substitution of one metal for the other metal in salts consists in transition of electrons from the more active metal (which substitutes for the less active metal) toward the ions of the less active metal which is thus replaced. These reactions are irreversible. If metal *A* displaces metal *B* from a solution of its salt, metal *B* will not displace metal *A* from the solution of its salt.

The Russian chemist N. Beketov arranged all metals in the series of their decreasing chemical activity in reactions where they displace one another from their salts. This series is known as the electrochemical series, and is

Ca, Na, Mg, Al, Zn, Cr, Fe, Ni, Pb, (H), Cu, Hg, Ag, Pt, Au

Any metal that stands in the series to the left will displace the metals, which follow it from solutions of their salts, but can only be displaced itself by the metals that come before it in the series.

Hydrogen is the only nonmetal that stands in the electrochemical series. It shares one property common to the metals, vis., the ability of forming positive ions. Hydrogen can therefore also displace some metals from their salts and can itself be displaced by many metals in acids:

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow + Q$$

The ionic equation for this reaction is

$$\overbrace{Zn^0 + 2H^+}^{\xrightarrow{2\bar{e}}} = Zn^{2+} + H_2\uparrow + Q$$

All the metals coming in the electrochemical series before hydrogen displace it from acid solutions, while all the metals that follow hydrogen, e.g. copper, do not displace it.

The reaction of displacement of one metal by another can be realized without bringing in contact the displacing metal with the solution of the salt

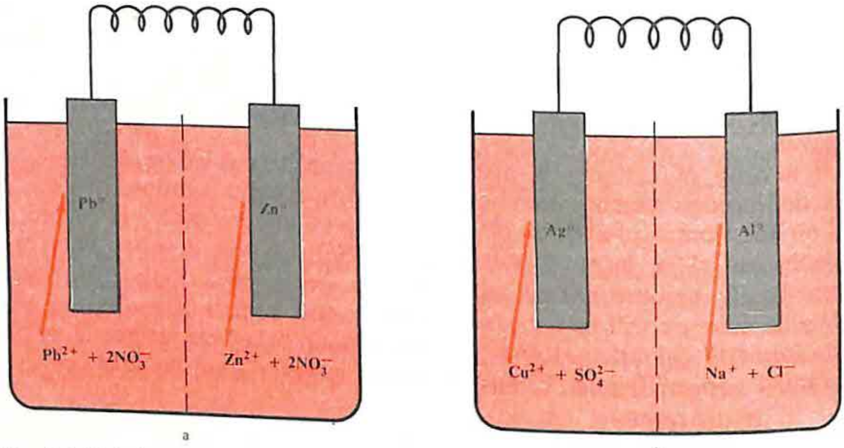


Fig. 5.4 Voltaic cells:
a–zinc-lead cell; *b*–aluminium-copper cell

of the other metal. Both metals, e. g. zinc and lead, can be immersed in solutions of their own salts separated by a porous membrane and connected by a metal wire as shown in Fig. 5.4. The reaction will be the same as if we placed zinc directly into the solution of the lead salt:

$$\overbrace{\mathrm{Zn}^0+\mathrm{Pb}^{2+}}^{2\bar{e}}=\mathrm{Zn}^{2+}+\mathrm{Pb}^0+Q$$

Zinc will dissolve in the right-hand compartment, i. e. it will pass in solution as the Zn^{2+} ion. Electrons that are eliminated from the zinc atoms pass into the lead plate through the wire. The ions of lead, contained in the solution, will be attracted to the plate and will capture the electrons furnished by zinc to turn into electrically neutral lead atoms. The lead plate will soon become covered with new layers of metallic lead. The anions of the acid residue will pass through the porous partition from the left compartment to the right one. The number of cations will thus decrease in the latter. Since the lead of the plate is not involved in the reaction, it can be changed for any other metal that does not react with lead salts. Carbon can be used for the purpose as well. The zinc salt is not involved in the reaction either*. It can therefore be replaced by any other electrolyte that does not react with zinc. Devices employing this principle are known to us from the physics course. They are called voltaic cells and are used as chemical sources of electric current. A voltaic cell can be made of any pair of metals immersed in solutions of their salts. The voltage across the poles of a cell will be the greater, the farther from each other the metals are separated in the electrochemical series.

---

* The solution of the zinc salt cannot be, however, replaced by pure water. Owing to the negligibly small number of ions (H^+ and OH^-), water virtually does not conduct electricity and the electric circuit shown in Fig. 5.4 will thus remain broken, and the voltaic cell would not work. The picture will be the same if we replace the porous membrane by a solid one.

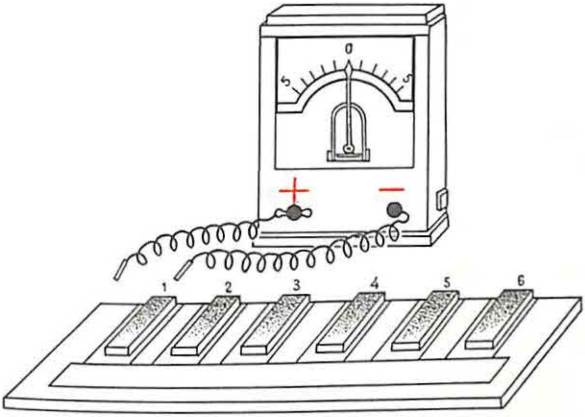


Fig. 5.5 Measuring electrode potentials:
1 – zinc; 2 – iron; 3 – nickel; 4 – lead; 5 – copper; 6 – silver

A device intended to measure the voltage that arises across the poles (the electrode potential) is shown in Fig. 5.5. The figure also shows strips of paper, impregnated in solutions of salts of various metals and placed on a glass plate. Metal plates are placed on top of each paper impregnated with the salt of the appropriate metal. A long strip of blotting paper is placed across the ends of the shorter strips, the long strip being impregnated in a solution of any electrolyte you may choose. When we touch any two metal plates with the wires leading to the voltmeter, the pointer of the instrument will deviate to indicate the voltage between them; the deviation being the greater, the farther the given metals stand from each other in the electrochemical series. The metal plates, and hence the paper strips impregnated in the solutions of their salts, are arranged in the experiment in the order in which the metals come in the electrochemical series.

Voltaic cells employing other types of oxidation-reduction reactions are also possible; the reaction of oxygen combination with hydrogen can also be used in a voltaic cell:

$$\overset{4\bar{e}}{\overbrace{2H_2+O_2}} = 2H_2O+Q$$

Let us now make a voltaic cell. Use a piece of aluminium, a piece of silver, two solutions, viz., copper sulphate and sodium chloride solution, a metal wire, and a vessel separated into two chambers by a porous membrane.

1. Using the electrochemical series, let us find which of the two metals will react with one of the two available electrolytes by the substitution mechanism. This metal is aluminium and the electrolyte is the solution of copper sulphate.

2. Place a piece of aluminium and the copper sulphate solution in separate chambers of the vessel.

3. Complete the voltaic cell by placing the other metal (silver) and the other electrolyte (NaCl) in the chambers of the vessel and connecting the metals by the wire. The device thus assembled is shown in Fig. 5.4 *b*.

The right-hand chamber of the cell will contain aluminium immersed in sodium chloride solution where it will dissolve to give its ions to the solution, while metallic copper will precipitate on the silver surface in the left-hand chamber.

Whether a metal can be found in the free state in nature or occurs in the form of its compounds can be established from the position of the metal in the electrochemical series. Metals coming before hydrogen occur in the Earth's crust only as their compounds. Metals coming after hydrogen in the electrochemical series, i.e. copper, mercury, and silver, mainly occur in nature as their compounds but they can also (in rare cases) be found in their native (free) state. The metals which complete the series, i.e. gold and platinum, occur mainly in their native state and only in rare cases in the form of their compounds.

?

1. The following are given: aluminium, tin, copper, mercury, silver, and the solutions of their salts. Write ionic equations for the reactions that can be realized between given metals and salts.

△

2. A vessel with a porous partition, a piece of zinc, coal, a copper wire, hydrochloric acid and zinc chloride solutions are given. Following the pattern in Fig. 5.4, make a voltaic cell from these materials and write ionic equations for the reactions that occur in both compartments of the cell. What is the difference between the results of this reaction when carried out in a Kipp generator and those of the reaction in a voltaic cell?
3. What energy conversions take place in a voltaic cell?

5.5

Electrolysis

The electric current arising in a closed circuit of a voltaic cell is the result of chemical reactions occurring in the cell. Let us now see what happens when electric current is not generated by a chemical reaction, but on the contrary, a chemical reaction is induced by an electric current.

Remember that in order to reduce a chemical element we must furnish electrons to its atoms or ions, and that in order to oxidize a chemical element, electrons must be eliminated from its atoms or ions. Both reduction and oxidation can occur not only in chemical reactions but also due to the action of an electric current.

Place copper(II) chloride solution into a U-tube (Fig. 5.6) and immerse the carbon electrode in each end. Connect the electrodes to the terminals of a storage battery: red copper will precipitate on the cathode and free chlorine will evolve at the anode (detectable by its odour). This indicates that the electric current has induced a chemical reaction in the copper(II) chloride solution decomposing the compound into copper and chlorine

$$CuCl_2 = Cu + Cl_2\uparrow \qquad (1)$$

Consider this reaction from the standpoint of the theory of electrons. A storage battery acts like an 'electron pump': it pumps electrons from one electrode to the other. The electrode from which the electrons are removed becomes charged positively. It becomes the anode. Meanwhile the electrode to which these electrons are furnished becomes negatively charged, i.e. it becomes the cathode.

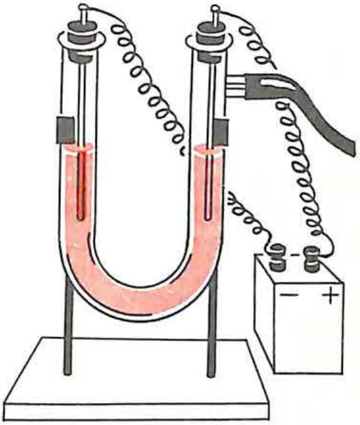


Fig. 5.6 Electrolyzer

Copper(II) chloride dissociates in the solution into copper(II) ions and chloride ions:

$$CuCl_2 = Cu^{2+} + 2Cl^- \qquad (2)$$

The random motion of ions becomes orderly when an electric current passes. Positively charged copper ions move towards the negative electrode (cathode), while negative chloride ions move toward the positive electrode (anode). When copper ions reach the cathode they take electrons from it, i.e. become reduced to neutral copper atoms:

$$Cu^{2+} + 2\bar{e} = Cu^0 \qquad (3)$$

Copper metal is deposited on the cathode surface. (The same will happen if any soluble copper salt is substituted for copper(II) chloride solution.) Chloride ions reach the anode to give off one electron each. By this process they are oxidized and turn into electrically neutral atoms which combine in pairs to form chlorine molecules

$$2Cl^- - 2\bar{e} = 2Cl^0, \quad Cl^0 + Cl^0 = Cl_2 \qquad (4)$$

(The same will happen at the anode if any soluble chloride is substituted for copper(II) chloride solution.)

If we now put together all left-hand parts of equations (2), (3) and (4) and then all their right-hand parts, and delete the recurring members from the resultant equation, the overall equation (1) will be obtained. (Check this.)

Oxidation-reduction reactions induced by electric currents are called electrolysis, i.e. decomposition by electricity (cf. hydrolysis and pyrolysis). The passage of electric currents through solutions or melts of electrolytes is always associated with electrolysis: reduction occurs at the cathode and oxidation at the anode.

The amount of energy required to discharge metal ions at the cathode depends on the position of the metal in the electrochemical series: the more to the right the metal stands in the series, the lower the energy required to reduce it. If the electric current passes through a mixture of electrolytes, the metals are reduced in the order reverse to their arrangement in the electrochemical series. If a solution contains cations Cu^{2+} and Ag^+, and if the solution is acidified, metallic silver will first be deposited at the cathode and then the copper will be deposited on silver. The hydrogen ions will be discharged at the cathode only after all Ag^+ and Cu^{2+} ions have disappeared from the solution.

Let us electrolyze a solution of potassium iodide in the U-tube. Immerse the electrodes in the solution, and add phenolphthalein to the cathode end of the U-tube and starch solution to its anode end. Pass an electric current through the solution: the cathode becomes covered with gas bubbles. This is hydrogen. The solution at the cathode will turn crimson to indicate the presence of an alkali, probably potassium hydroxide KOH. The solution near the anode will turn blue to indicate the liberation of free iodine. The electrolysis of potassium iodide solution gives three products, viz., hydrogen and potassium hydroxide which are liberated at the cathode, and free iodine, which is evolved at the anode.

During electrolysis of copper(II) chloride metal (copper) is liberated at the cathode, while in the last case when we electrolyzed potassium iodide solution, hydrogen and not the metal (potassium) was liberated at the cathode. Why?

Let us consider the following reactions (their equations are numbered) that occur during the electrolysis of an aqueous solution of potassium iodide:

$$2KI = 2K^+ + 2I^- \quad (I)$$

$$\begin{array}{cc} | & | \\ \text{cathode} & \text{anode} \\ \downarrow & \downarrow \\ 2K^+ & 2I^- - 2\bar{e} = 2I^0 \quad (III) \end{array}$$

$$2H_2O \rightleftarrows 2H^+ + 2OH^- \quad (II)$$

$$2H^+ + 2\bar{e} = 2H^0 \quad (V) \qquad 2I^0 = I_2 \quad (IV)$$

$$2H^0 = H_2\uparrow \quad (VI)$$

Potassium iodide dissociates (I) into the K^+ and I^- ions. The potassium cations move toward the cathode and the iodide ions to the anode. Water also dissociates (II) into ions but the degree of dissociation is very low. Ions of four types are therefore present in the solution: potassium cations K^+, hydrogen cations H^+, iodide anions I^-, and hydroxyl ions OH^-. All ions in the solution are involved in the conduction of electricity, but the main role in the process belongs to the dominant ions in the solution. In our case these are the potassium ions K^+ and the iodide ions I^-. Those ions which require least energy are discharged at the electrodes, even though their concentration in solution may be low. The iodide ions give off the electrons more easily than the hydroxyl ions. The iodide ions are therefore oxidized at the anode (III), giving off their electrons. The liberated iodine atoms combine in pairs to form I_2 molecules (IV).

According to the position in the electrochemical series, hydrogen ions accept electrons easier than potassium ions. Potassium ions that move to the cathode during electrolysis will therefore accumulate at the cathode but will not discharge. Hydrogen ions will capture electrons at the cathode (V), i.e. they will be reduced. Hydrogen atoms will then combine in pairs to form H_2 molecules (VI). The concentration of hydrogen ions in our solution is very low, but it does not decrease at the cathode because new water molecules fall into H^+ and OH^- ions immediately and the H^+ ions are therefore constantly discharged at the cathode. The hydroxyl ions are accumulated simultaneously at the cathode. If we now put together all left-hand parts and separately all right-hand parts of equations I through VI, and then delete the recurring members, the following overall equation will be obtained:

$$2KI + 2H_2O = \underbrace{H_2 + 2KOH}_{\text{at the cathode}} + \underset{\text{at the anode}}{I_2}$$

Acid residue ions will be oxidized at the anode during electrolysis of aqueous solutions of binary acids and their salts (except HF), and the hydroxyl ions during electrolysis of higher oxyacids and their salts.

The following conclusions can be drawn from what has been said: only electrolytes soluble in water, or molten electrolytes can be electrolyzed. The electrolysis of electrolyte solutions is easier than that of their melts because electrolytes (salts and alkalis) melt at very high temperatures. But not all elements can be obtained in the free state by the electrolysis of aqueous solutions of their compounds. The alkali metals, for example, cannot be obtained by this method. They are obtained by the electrolysis of their melts.

?

1. What processes occur during the electrolysis of aqueous solutions of (a) hydriodic acid, and (b) potassium chloride?

△

2. A steel object and a carbon rod were immersed in a solution of nickel(II) chloride $NiCl_2$. The steel object was connected by a wire to the negative pole of a storage battery and the carbon rod to the positive pole. The steel object became coated with a layer of nickel. What reactions occurred during electrolysis of nickel chloride solution? What is the practical result of this electrolysis?
3. Three valuable products are obtained in industry by electrolysis of an aqueous solution of sodium chloride. What are these products? Draw a diagram of the electrolysis using the diagram for the electrolysis of potassium iodide as a pattern.

5.6

Practical Uses of Electrolysis

Much of the energy produced at electric power stations is consumed by chemical and metallurgical industries.

Most active metals (e.g. the alkali metals) and also most active nonmetals (the halogens) occur in nature only in the form of their compounds in which metals are present as positive ions (cations) and nonmetals as negative ions (anions). In order to isolate the metal from these compounds the missing electrons have to be given back to its ions, and in order to obtain the nonmetal, excess electrons must be taken from its ions, e. g.:

$$Na^+ + \bar{e} = Na^0,$$

$$2F^- - 2\bar{e} = 2F^0, \quad 2F^0 = F_2$$

This can be done by electrolysis. Electrolysis is the only method by which fluorine can be isolated in the free state and the only advantageous method by which most chemically active metals can be obtained. Electrolysis is therefore used in industry to prepare fluorine, chlorine, and most active metals, including aluminium.

Electrolysis is also used for electroplating (chome- and nickel-plating). To that end an article to be plated with nickel or chromium is placed in a bath containing a solution of the corresponding nickel or chromium compound, and the article is connected to the negative pole of a source of direct current. The article is kept in the bath until nickel or chromium coat of the required thickness is deposited on its surface. This treatment improves the appearance of articles (the surface has a yellowish tint in nickel-plated articles and a bluish tint in chrome-plated articles), and also protects them from corrosion.

Electrolysis is used to deposit metals on articles with intricate shapes. The deposited metal is then removed and an accurate imprint of the article is thus obtained. Obtaining relief by electrolysis is called galvanoplastics. This technique was invented by the Russian scientist S. Yakobi.

△ Describe some of the practical uses of electrolysis that you know.

5.7 Alloys

Metals are simple substances that resemble one another because of the presence of metallic bonding and, in some cases, because they have the same type of crystal lattice. Metallic bonding can be established not only between positive ions of one metal but between different metals as well. Metals can therefore form alloys. Nonmetals can, however, also be alloyed with metals in some cases.

Alloys rather than metals are normally used in technology because metals in most cases do not possess the useful properties that are otherwise attained in alloys. Aluminium is light but its hardness if low. In order to increase the hardness of aluminium it is alloyed with copper, manganese, and magnesium to obtain duralumin. Gold is beautiful but very ductile, and articles made of pure gold are easily deformed and abraded. In order to avoid this, gold is normally alloyed with copper in jewelry.

Alloys are solid solutions in most cases. They are called so because after their crystallization from a melt, the ions of various components remain distributed as uniformly as they were in the melt.

If ion dimensions of the metals are about the same and their crystal lattices are identical, *substitutional solid solutions* are formed in which ions of one metal are partly replaced by the ions of the other metal at points of the

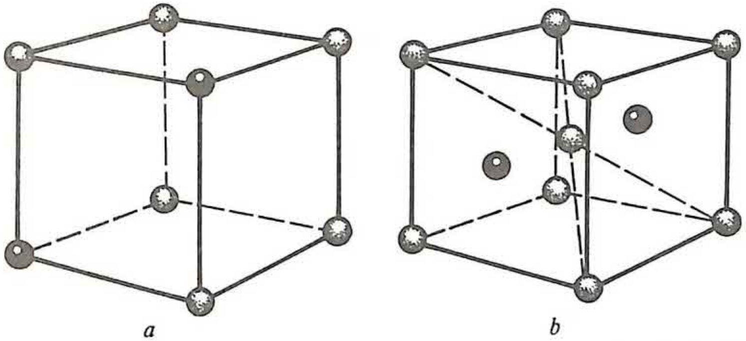


Fig. 5.7 Replacement of metal ions in alloys (*a*); ions of one metal enter the interstices of the other (*b*)

crystal lattice (Fig. 5.7*a*). Examples of substitutional solid solutions are alloys of copper with nickel (nickel silvers), and of copper with aluminium.

If ions of one metal or atoms of a nonmetal in an alloy are significantly smaller than the ions of the other metal, an *interstitial solid solution* is formed (Fig. 5.7*b*). The smaller particles in such solutions enter the interstices formed between the positive ions of metal at the points of the crystal lattice during crystallization of the alloy. Steel, which is an alloy of iron and carbon, is an interstitial solid solution.

Some alloys contain chemical compounds of their components in the form of inclusions. Such compounds in alloys are formed by magnesium and lead, magnesium and zinc, aluminium and carbon, iron and carbon, etc.

Some metals form uniform alloys in the liquid state, but crystallize separately when the liquid cools. Their solid alloy is therefore a mechanical mixture of crystals of different metals. These alloys are very strong but melt at low temperatures. Solder consisting of tin and lead is such an alloy.

Why do alloys have properties that are different from the original metals from which they are formed?

An alloy would normally have lower electrical conductivity and heat conductivity than the metals in the pure state. This can be explained by the presence in the alloy of ions of different metals that interfere with movement of free electrons. Alloys are usually harder and less ductile than the original metals. This is due to the different sizes of ions of metals that form the alloy. The larger ions of one metal enter the crystal lattice of the other metal and tend to expand it while the smaller ions tend to compress it. In both cases a certain strain arises in the alloy that increases its hardness and decreases its ductility.

?
△

1. Alloys rather than pure metals are used in industry. Why?
2. What types of alloys do you know?
3. In what cases (a) substitutional and (b) interstitial solid solutions are formed in alloys?
4. In what cases alloys with the structure of a mechanical mixture are formed?

5. Iron and chromium crystallize in the same lattice. The atomic radius of iron is 0.13 nm and that of chromium, 0.13 nm. What type of alloy do they form?

6. How do hardness, ductility, electrical and heat conductivity change in the transition from metals to their alloys? Explain these changes.

5.8 Corrosion of Metals

Articles made of metals or their alloys (except gold and platinum) are destroyed by air, atmospheric precipitation, moisture of the soil, to form compounds stable to the environmental effects. Metals in chemical apparatuses are attacked especially badly, because they are exposed to the action of oxygen, acids, alkalis, and other aggressive media; moreover these harmful effects are often increased at elevated temperatures and pressures.

The destruction of metals and their alloys due to the chemical interaction with the environment is called corrosion (from Latin *corrodere* to gnaw).

Corrosion impairs the quality of metal articles and structures, and with time they become completely worn out and useless. With the growing use of metal structures and machines in industry, transport, and agriculture, protecting metals from corrosion becomes especially important. Longer service lives of machines and structures increases the economic potential of the country and speeds up her successful march toward communism. Corrosion control is therefore an extraordinarily important problem. But in order to be successful in fighting corrosion, we must study this process in detail.

The corrosion of metals is an oxidation-reduction process in which the metal atoms are oxidized to ions, e. g.:

$$\mathrm{Fe} - 2\bar{e} = \mathrm{Fe}^{2+}$$

$$\mathrm{Cu} - 2\bar{e} = \mathrm{Cu}^{2+}$$

What promotes and what inhibits corrosion? Let us establish this experimentally.

Iron is known to corrode under the action of oxygen and water. Place an iron nail in a test tube, add water to the full capacity, close the mouth with your thumb, turn it upside down and place the test tube in a dish (or other container) filled with water, and release the finger. Now displace the water from the test tube by oxygen. Proceed in the same way with other test tubes and nails but use sodium chloride solution instead of water. Add sodium hydroxide to one solution. Before placing the nails into the test tubes, wind a copper wire round one nail, and attach a zinc strip to another. Allow the test tubes to stand for a while. In about 24 hours the picture in the test tubes will be as shown in Fig. 5.8. The captions in the figure indicate which metal is being tested in each particular case (iron alone, iron with copper, iron with zinc) and which medium is being tried (water, sodium chloride solution, sodium chloride solution containing some sodium hydroxide). The judgement concerning the corrosion can be drawn from the volumes of spent oxygen (by the level to which the liquid rises in the test tube), and from the character of the corrosion product precipitated in solution.

Compare the results of the experiment in test tubes 2 and 3. Iron was exposed to the action of the same solution, but in one case it was in contact with copper. Corrosion occurred in both cases and brown ferric hydroxide precipitated in both glasses, but the amount of rust in experiment 2 is smaller than that in experiment 3. The amount of oxygen consumed in experiment 2 was accordingly smaller than that in experiment 3 (the level of the liquid in test tube 2 rose insignificantly). Hence the corrosion of iron is increased significantly if it comes in contact with copper.

Now compare the resulst of experiments in test tubes 2 and 4. The iron was placed in the same solutions but in one case it was in contact with zinc. Corrosion occurred in both experiments but in test tube 2 the precipitate is

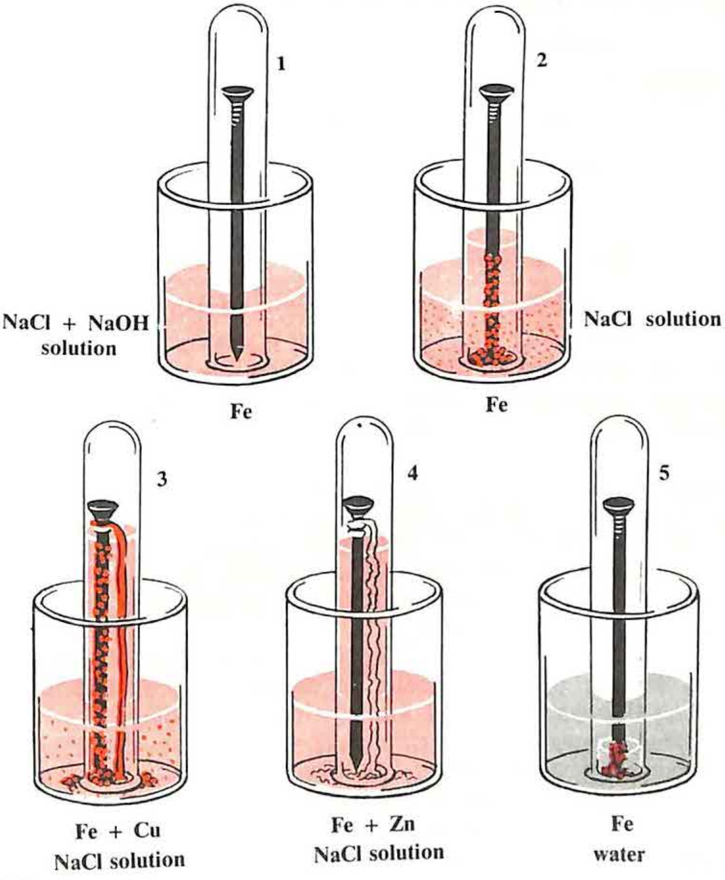


Fig. 5.8 Metal corrosion

brown (rust) while in test tube 4 the precipitate is white and a great deal of it. It is zinc hydroxide and this means that zins, and not iron, corroded in test tube 4. We can conclude that iron practically does not corrode when it comes in contact with zinc.

Intensification of the corrosion by copper and its inhibition by zinc is explained by the formation of galvanic couples like those in voltaic cells. When iron comes in contact with zinc, a voltaic cell is formed in which the zinc is a more active metal and it will be oxidized into Zn^{2+} ions, whereas the electrons eliminated from its atoms will flow towards the iron surface where the hydrogen ions, contained in the solution surrounding the metal, will be reduced. Hydrogen will either be liberated in the free state from the iron surface or its atoms will be oxidized into water by oxygen dissolved in water. The latter reaction is more likely to happen.

When iron is in contact with copper, another galvanic couple is formed but the more active metal is now iron and it will be oxidized. The following reactions will occur in the solution that comes into contact with the metals:

$$2H_2O \rightleftarrows 2H^+ + 2OH^-$$

on the surface

of iron	of copper
$Fe^0 - 2\bar{e} = Fe^{2+}$	$2H^+ + 2\bar{e} = H_2$

The reaction in the water film will be

$$Fe^{2+} + 2OH^- = Fe(OH)_2 \downarrow$$

$$Fe(OH)_2 + O_2 + H_2O \rightarrow Fe(OH)_3 \downarrow$$

The corrosion of a metal increases sharply if it is in contact with any other less active metal, i. e. the metal to its right in the electrochemical series. But the corrosion is markedly inhibited if the metal comes in contact with a metal that stands to its left in the electrochemical series, i. e. a more active metal.

Compare the results of experiments in test tubes 1 and 2. The addition of sodium chloride to water intensified the corrosion of the iron: a significant amount of rust was produced and much oxygen was consumed in the reaction. When sodium hydroxide was added to the sodium chloride solution in test tube 5, the corrosion was retarded: the amount of rust was small and not much oxygen was consumed.

We can thus conclude: the rate of corrosion of a given metal depends firstly on whether or not it comes in contact with another metal, and secondly on the composition of the solution surrounding it.

Some components of the surrounding medium, e. g. the chloride ions, intensify corrosion, while others can retard corrosion. For example, the corrosion of iron is retarded in the presence of hydroxyl ions.

Metal structures corrode more quickly in coastal areas. This is explained by the presence in the sea water of the chloride ions. Splashes of sea water are evaporated in the air to liberate crystals of salt. These precipitate on metallic structures and dissolve in the film of water that is present on them. The chloride ions then attack the metal.

Now we can understand the measures taken everywhere to prevent corrosion.

The greater the difference in the chemical activity of two contacting metals, the stronger the corrosion of the more active and the more effectively the less active metal is protected from corrosion. Copper parts should therefore be absent in aluminium structures (see the position of aluminium and copper in the electrochemical series). If this is unavoidable, the contact between these metals should be neutralized as much as possible by applying lacquers and varnishes to their surfaces. The protective action of more active metals on less active ones is utilized in the prevention from corrosion of underground pipe systems and in sea-going ships. Ingots of alloys of magnesium or zinc which are quite active are attached to underground pipes and lowered into the sea water by sides of ships during long moorage.

To prevent corrosion of metal articles, they are insulated from the environment by coats of lacquers, varnishes, lubricants, protective coats of other metals, etc. The protective coating should be stable to the action of a given environment, it should be sufficiently strong and adhere to the metal.

In some cases the rate of corrosion can be significantly decreased by adding small amounts of reagents to the liquid environment, which would promote the formation of a protective film on the metal's surface; they are called *inhibitors*. Organic inhibitors are widely used. Adding them to hydrochloric acid, for example, helps store and ship the acid in steel containers (instead of brittle carboys). Hydrochloric acid containing inhibitors is used to clean metal surfaces from rust or scale. Metal oxides are dissolved in it while the metal itself is not. In order to prevent corrosion, oxygen should be removed from boiler water.

?
△

1. How will the corrosion process in experiment 4 change if we place a strip of zinc into the test tube so that it does not touch the nail? Explain your answer.
2. What methods do you know to control corrosion?

■

3. Make a list of household articles made of metals and their alloys. Indicate in each case the special physical property of the metal or its alloy that accounts for the use of this article. Do not forget mirrors, thermometers, or electric bulbs. Indicate cases of corrosion, if any.

6 Metals of the Main Subgroups of the Periodic System

6.1 The Alkali Metals

Let us continue studying separate chemical elements. We shall begin with metals which have the most pronounced metallic character. These are the alkali metals. They form the main subgroup of group I of the periodic system. The atoms of the alkali metals contain one valency electron. As they give it off, their atoms turn into single-charged positive ions. The alkali metals are monovalent in all their compounds. They form only ionic bonds. The alkali metals are the most active metals: stand the first in the electrochemical series. Hydroxides of the alkali metals, including the known sodium hydroxide NaOH (caustic soda) and potassium hydroxide KOH (caustic potash), are hazardous. They burn skin and destroy textiles. Hence their name caustic (from the Greek *kaustikos* to burn). Like hydroxides, all salts of the alkali metals are soluble in water. All of them are strong electrolytes.

Each alkali metal gives its specific colour to flame. In order to identify an unknown compound of alkali metal it should be put into the flame of a burner at the point of an iron wire or some other pointed object (Fig. 6.1). The yellow colour of the flame is specific to sodium, while potassium compounds colour the flame pale violet.

The wire should preliminarily be calcined till it does not colour the flame yellow, i.e. until sodium compounds are evaporated from its surface. If we rub the calcined wire with the fingers and introduce it into the flame again, the yellow tint of the flame will reappear, because the human skin is always soiled with sodium compounds. The experiment proves it.

The yellow luminescence of sodium vapour was used during the flight of one of the Soviet space rockets, when it was necessary to locate it in the space; sodium vapour was discharged from it by command from the earth.

The radii of atoms of the alkali metals increase with their atomic numbers. The distance from the outer (valency) electron to the nucleus increases and the bond gradually weakens, to become the weakest in cesium. Electrons are easily knocked out when the surface of the metal is illuminated, and electric current is thus generated in devices similar to those shown in Fig. 6.2. These devices are connected with switches that turn on or off electric current. They are used in automatic devices controlled by light pulses without human involvement.

Solubility of hydroxides of alkali metals increases with their atomic number because the distance between ions of the alkali metal and hydroxide

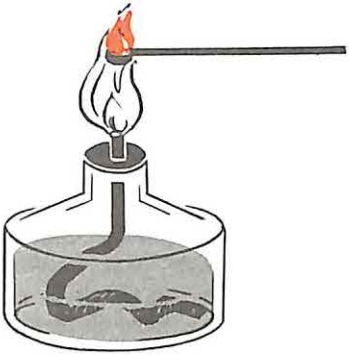


Fig. 6.1 Flame test

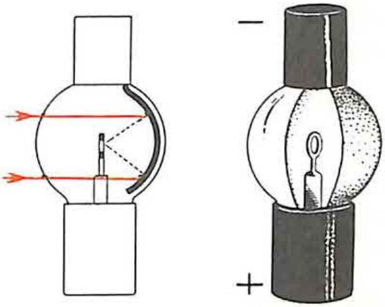


Fig. 6.2 'Electric eye': a section and a general view.

Incident light beams are shown in solid and electrons knocked out from cesium, in a broken line

ions in the crystal lattice increases with increasing atomic radii to weaken mutual attraction of these ions.

?

1. Characterize the position of the alkali metals in the periodic system and in the electrochemical series, describe their atomic structure and chemical properties.

△

2. Why and how does the chemical activity of the alkali metals change with their increasing atomic number?
3. Characterize the general properties of hydroxides and salts of the alkali metals.
4. The flame of a burning hydrogen jet is colourless if the gas-outlet tube is made of iron, and yellow if the tube is made of glass. What does the yellow colour of the flame indicate?
5. Write down ionic equations for reactions between sodium and (a) water and (b) hydrochloric acid.
6. Explain why the alkali metals, their oxides or hydroxides do not occur in nature. Salts of the alkali metals only occur. Where do they accumulate with time? Write ionic equations for reactions involving alkali metals, their oxides or hydroxides if these substances appeared in the Earth's crust. (Use sodium as an example.)

6.2 Natural Compounds of Alkali Metals and Their Uses

Compounds of sodium and potassium are only abundant, while the other alkali metals are rare elements. The most important sodium compound is sodium chloride known as table or common salt. Sodium chloride is obtained in this country from salt lakes and from deposits. Bays and gulfs of seas separated in prehistoric times from the sea to turn into lakes, which then dried to precipitate salt. Deposits of rock salt were thus formed.

Sodium chloride is the vital salt which we take with food. It was valued much in the past times; lack of salt was the cause of 'salt mutinies' and uprisings; lumps of salt were used as money in some countries.

Sodium chloride is contained in all tissues of our body. In profuse blood loss, and in diseases during which salts are removed from the body, physiological solution is administered. This is actually a 0.9 per cent solution of sodium chloride.

Table salt is taken mainly with animal food, but its content is low. Therefore we add salt to our food, especially to vegetable food. Animals also need salt. Wild animals lich salty soils. Salt is added to the feed of domestic animals. Table salt is used to can foods (to prevent putrefaction). Salted meat, fish, and vegetables can be stored for longer time because when contained in increased concentrations salt kills putrefactive microbes.

Large amounts of sodium chloride are used in chemical industry for the manufacture of sodium hydroxide NaOH, soda Na_2CO_3, and other sodium compounds.

Sodium hydroxide and soda are important materials for the chemical industry. They are used to purify petroleum products from acids, and to convert vegetable and animal fat into soap. Soda is used in the manufacture of glass; in the house it is used for laundry and other purposes.

Common salt, soda, soap, and glass are among the most important compounds of sodium that are used in everyday life. Sodium, that is contained in window glass, in a cake of soap, and also in our blood, was earlier contained in the water of the ocean. A deposit of the salt was formed on the bottom of the ocean, and table salt was then extracted from this deposit. Table salt is taken by man with food or used at chemical plants where it is converted into soda, soda is converted into soap, glass, and other consumer goods. Soda has become an important raw material for the chemical industry. A small proportion of soda is only used as the finished product, while its main bulk is consumed in the manufacture of other products.

Potassium salts are mainly used as mineral fertilizers.

△ 1. Describe the properties and specify the uses of sodium chloride, sodium hydroxide, soda, and potassium salts.

■ 2. Think of the many important uses of sodium compounds. Table salt, glass, soda, soap, detergents, etc., are among these compounds. Take a wire or a pin, attach a small piece of soap at its point, and introduce into the flame. This may be the flame of a domestic gas stove or an oil lamp. The soap will take flame and burn to the end. If we continue holding the wire in the flame we shall see that the flame becomes bright yellow due to sodium that was contained in the soap.

Traces of sodium can be detected on our skin. Before washing hands, rub the calcined end of a pin with your fingers, and introduce the pin in the flame: it turns yellow.

3. Show diagrammatically the chain of conversions of table salt (described at the end of this section), that was once contained in the ocean, into materials and products we deal with in everyday life. Try to make the diagram graphic and picturesque.

6.3 General Properties of Elements of the Main Subgroup of Group II of the Periodic System

This group includes beryllium, magnesium, calcium, strontium, barium, and radium. They are called the *alkaline-earth metals.* The greatest similarity in the properties of these elements is found in calcium, strontium, and barium. Radium differs from all other alkaline-earth metals by its special property which is called *radioactivity.*

The outer layer of atoms of these elements contains two electrons which are readily given off in chemical reactions. The oxidation number 2+ is therefore characteristic of these elements in compounds.

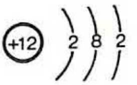
The simple substances formed by the elements of the main subgroup of group II are typical metals. Compared with the alkali metals, they are much stronger in the solid state and melt at significantly higher temperatures. All alkaline-earth metals except radium are light.

The simple substances of these elements react actively with nonmetals, water, acids. The properties of beryllium differ significantly from the properties of the other alkaline-earth metals. Beryllium is stable to atmospheric oxygen, it does not react with water, but reacts with alkalis.

Except beryllium, whose compounds are amphoteric, all other alkaline-earth metals form basic oxides and hydroxides (bases).

6.4 Magnesium

The chemical symbol of magnesium is Mg, its atomic number is 12, and the atomic weight 24. The diagram of its atomic structure is



Magnesium is a silvery-white light metal melting at 651 °C. At ordinary temperatures magnesium is protected from oxidation by an oxide film that is formed on its surface. When heated, this film is destroyed and magnesium burns with an intense white light to form white smoke which is actually its oxide

$$\overbrace{2\text{Mg}+\text{O}}^{4\bar{e}}{}_2=2\text{MgO}+Q$$

Magnesium nitride Mg_3N_2, which is formed during the interaction of magnesium with the nitrogen of the air, is admixed to magnesium oxide.

Place magnesium shavings on a metal gauze and ignite them. Place the burning magnesium into water (Fig. 6.3): the flame is not extinguished but, on the contrary, is intensified. Magnesium burns in water vapour by combining with oxygen of the water:

$$\text{Mg}^0 + \text{H}_2^{1+}\text{O}^{2-} = \text{Mg}^{2+}\text{O}^{-2} + \text{H}_2^0\uparrow$$

A pale flame of burning hydrogen can be seen over magnesium burning in the water vapour. Water becomes cloudy from particles of magnesium oxide that accumulate in it. Add phenolphthalein: the solution remains colourless

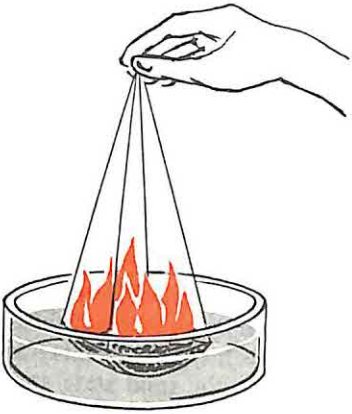


Fig. 6.3 Magnesium burning in water vapour

for a while but then turns crimson. Magnesium oxide combines with water to form magnesium hydroxide

$$MgO + H_2O = Mg(OH)_2$$

while magnesium hydroxide dissolves partly in water to dissociate into magnesium ions and the hydroxide ions:

$$Mg(OH)_2 \rightleftarrows Mg^{2+} + 2OH^-$$

This equation shows that equilibrium is established between the dissolved Mg^{2+} and OH^- ions and solid magnesium hydroxide.

Unless magnesium burns, it does not react with cold water; but the reaction begins in boiling water

$$\overbrace{Mg + 2H_2O}^{2\bar{e}} = Mg(OH)_2 + H_2\uparrow + Q$$

Magnesium displaces hydrogen from acid solutions:

$$Mg + 2HCl = MgCl_2 + H_2\uparrow$$
$$Mg + H_2SO_4 = MgSO_4 + H_2\uparrow$$

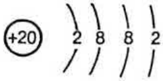
Magnesium reduces less active metals and is therefore used in metallurgy.

Magnesium is also used in the manufacture of various alloys (elektron, duralumin, magnalium, etc.). It is a constituent of light alloys that are widely used in automobile and aircraft building, various tools, and instruments.

Mixtures of powdered magnesium with oxidants are used in pyrotechnics (flares), for illuminating purposes (flash photography), as igniting primers in incendiary devices.

6.5 Calcium

The chemical symbol is Ca, its atomic number 20, its atomic weight 40, and the structure of the atom



Calcium is a light silvery-white metal. In their chemical properties calcium and the other alkaline-earth metals are close to their neighbours in the main subgroup of group I, the alkali metals. This similarity is due to their atomic structure. The atom of the element standing in the main subgroup of group II differs from the atom of the neighbouring alkali metal in one unit of the positive nuclear charge and a distinguishing electron in the outer layer.

If we heat a piece of calcium it will burn with a brick-red flame and a white smoke, which actually consists of the finest solid particles of calcium oxide CaO:

$$\overbrace{2\mathrm{Ca}+\mathrm{O}}^{4\bar{e}}{}_2 = 2\mathrm{CaO} + Q$$

When dropped in water, calcium reacts with it to turn into calcium hydroxide and to displace hydrogen from water:

$$\overbrace{\mathrm{Ca}+2\mathrm{H}}^{2\bar{e}}{}_2\mathrm{O} = \mathrm{Ca(OH)}_2 + \mathrm{H}_2\uparrow + Q$$

Phenolphthalein colours the obtained solution crimson. This confirms our conjecture about similarity of calcium to the alkali metals: like the alkali metals it reacts with water to liberate hydrogen. Like hydroxides of the alkali metals, the hydroxide of calcium dissolves in water, i.e. it is the alkali.

Calcium would normally be kept under kerosene because it can react with water vapour contained in the air.

6.6 Magnesium and Calcium Compounds

Higher oxides of magnesium and calcium have the general formula RO. In ordinary conditions MgO and CaO are colourless crystals or high-melting powders. The oxides of magnesium and calcium readily react with water. When water is added to calcium oxide energy is evolved and the water boils. Lumps of calcium oxide adsorb water and swell (Fig. 6.4) to turn into loose powdered calcium hydroxide:

$$\mathrm{CaO} + \mathrm{H_2O} = \mathrm{Ca(OH)_2} + Q$$

In industry this reaction is known as *slaking of lime*, calcium oxide is called *burnt* or *quicklime*, and calcium hydroxide, *slaked* or *caustic lime.*

Calcium oxide is prepared in industry by roasting limestone:

$$\mathrm{CaCO_3} = \mathrm{CaO} + \mathrm{CO_2}\uparrow - Q$$

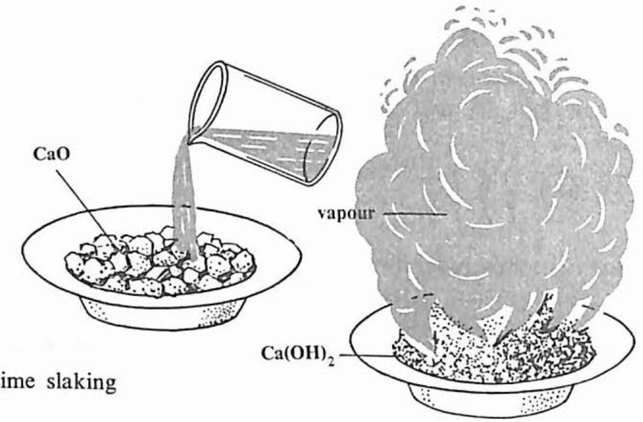


Fig. 6.4 Lime slaking

Oxides of magnesium and calcium are basic oxides and they combine with carbon dioxide to turn into carbonates

$$MgO + CO_2 = MgCO_3 + Q$$

$$CaO + CO_2 = CaCO_3 + Q$$

The general formula of hydroxides of magnesium and calcium is $R(OH)_2$.

Magnesium hydroxide is a white solid sparingly soluble in water, it enters exchange reactions with acids

$$Mg(OH)_2 + 2HCl = MgCl_2 + 2H_2O$$

$$Mg(OH)_2 + H_2SO_4 = MgSO_4 + 2H_2O$$

Calcium hydroxide is slightly soluble in water. Its aqueous solution is called *lime water*. Calcium hydroxide in lime water fully dissociates into ions, and a state of equilibrium is established between precipitated calcium hydroxide and dissolved Ca^{2+} and OH^- ions:

$$Ca(OH)_2 \rightleftarrows Ca^{2+} + 2OH^-$$

If calcium hydroxide is added to water in amounts greater than can be dissolved in the given volume of water, a white suspension of calcium hydroxide in lime water is formed. The suspension is called *milk of lime*.

A paste formed by calcium hydroxide with water, into which sand is added, is used as mortar to bind bricks and cover walls. As the paste adsorbs carbon dioxide from the air it sets into a very hard mass which is actually stronger than bricks themselves, for when old buildings are destroyed, cracks would often pass through bricks rather than through the mortar. The reaction of setting is as follows

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$

Carbonates are practically most important naturally occurring salts of magnesium and calcium.

Add phenolphthalein to lime water (the solution colours crimson). Now pass carbon dioxide from a Kipp generator: the clear solution first turns cloudy from precipitated calcium carbonate $CaCO_3$ which is insoluble in water:

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$

The ionic equation is

$$Ca^{2+} + 2OH^- + CO_2 = CaCO_3\downarrow + H_2O$$

When phenolphthalein turns colourless, the reaction is completed. All alkali is spent in the reaction and no OH^- ions are present in solution any longer.

Continue the experiment. Pass carbon dioxide again: cloudiness vanishes, which indicates that calcium carbonate has turned into a soluble compound. What is the composition of this new compound?

Carbon dioxide combines with water to form carbonic acid:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

The acid reacts with calcium carbonate:

$$CaCO_3 + H_2CO_3 = Ca(HCO_3)_2$$

A water-soluble calcium bicarbonate is formed and the solution thus becomes clear. The ionic equation of this reaction is

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^-$$

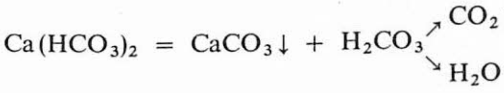
When magnesium carbonate reacts with water saturated with carbon dioxide, the former dissolves to give magnesium bicarbonate

$$MgCO_3 + H_2O + CO_2 = Mg(HCO_3)_2$$

The ionic equation for this reaction is

$$MgCO_3 + H_2O + CO_2 = Mg^{2+} + 2HCO_3^-$$

Heat the obtained solution of calcium bicarbonate: it turns cloudy again because the reverse reaction occurs, during which calcium carbonate is formed



$$Ca(HCO_3)_2 = CaCO_3\downarrow + H_2CO_3 \begin{matrix} \nearrow CO_2\uparrow \\ \searrow H_2O \end{matrix}$$

Magnesium bicarbonate decomposes by the same mechanism.

The above reactions are very important in nature. Rain water dissolves carbon dioxide contained in the air, passes through the soil and reacts with lime to dissolve it as the bicarbonate. This reaction is especially frequent in limestone deposits. When such water emerges to the surface it evaporates to precipitate calcium carbonate. As a result, beautiful icicles, known as stalactites, are formed in caverns which hang from their roofs (Fig. 6.5).

In addition to calcium carbonate, gypsum $CaSO_4 \cdot 2H_2O$ is another important calcium salt. When heated moderately, gypsum liberates 3/4 of

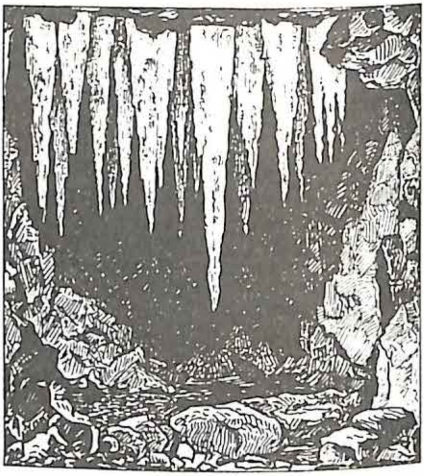


Fig. 6.5 Stalactites

crystallization water and turns into a white powder of semihydrate gypsum $2CaSO_4 \cdot H_2O$

$$2(CaSO_4 \cdot 2H_2O) = 2CaSO_4 \cdot H_2O + 2H_2O$$

When this powder is mixed with water, the reverse reaction occurs:

$$2CaSO_4 \cdot H_2O + 2H_2O = 2(CaSO_4 \cdot 2H_2O)$$

A mixture of semihydrate gypsum with water (of paste consistency) hardens in air for which gypsum is used to make stucco and statues. When mixed with slaked lime, gypsum is used for wall plastering; in surgery it is used to make immobilizing bandages in bone fractures.

Gypsum is slightly soluble in water. When temperature increases over 60°C its solubility does not increase but decreases. Gypsum can therefore be found in household kettles where it is deposited as scale.

?
△

1. Compare the properties of calcium (in the free state) and the alkali metals. Give the molecular and ionic equations for the corresponding reactions. Calcium is a light and strong metal. Why is it not used in aircraft building?
2. Compare the properties of magnesium (in the free state) with that of calcium. Which of their properties are similar and which are different?
3. Describe the properties of calcium oxide. How is it obtained in industry?
4. Describe the properties of calcium hydroxide.
5. Describe the properties and uses of gypsum.
6. How can a freshly prepared lime water be kept till the next lesson?
7*. Two test tubes contain equal amounts of lime water. Carbon dioxide is passed through one of them till the precipitate dissolves. The two portions are then mixed. What happens? Will the obtained mixture conduct electricity? Give molecular and ionic reaction equations.

8. What changes does slaked lime undergo in newly built houses and why do new houses remain 'damp' until these conversions are completed?

9. Write equations for the reactions by which the following conversions can be realized:

$$\begin{tikzcd}
 & \mathrm{MgO} \arrow[r] & \mathrm{MgCl_2} \arrow[dd] \\
\mathrm{Mg} \arrow[ur] \arrow[dr] & & \\
 & \mathrm{Mg(OH)_2} \arrow[r] & \mathrm{MgSO_4}
\end{tikzcd}$$

Specify the necessary conditions for each reaction.

10. Write the reaction equations for the following conversions:

$$CaCl_2 \rightarrow Ca \rightarrow CaO \rightarrow Ca(OH)_2 \rightarrow CaCO_3 \rightarrow$$
$$\rightarrow Ca(HCO_3)_2 \rightarrow CaCO_3 \rightarrow CaCl_2$$

Specify the conditions for the reactions.

11*. Chemical elements A, B, and C are given. A compound of A and B dissolves in water and litmus turns blue in the solution. A compound formed by all the three elements is insoluble in water, but becomes soluble if a compound of B and C is added to it simultaneously with water. Name the elements A, B and C, and the compounds that they form in our problem. Write the corresponding reaction equations.

12*. How will luminescence of a lamp (Fig. 1.2) change if carbon dioxide is passed through lime water?

6.7 Magnesium and Calcium Compounds in Nature and Their Uses

Magnesium is a part of very many minerals, among which the main are magnesite $MgCO_3$, dolomite $MgCO_3 \cdot CaCO_3$, and carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$.

Magnesite and dolomite are used in the manufacture of refractory materials, and also for obtaining free magnesium.

Carnallite can be the source of free magnesium as well, but it is also used as a fertilizer which is added to soil to furnish magnesium and potassium to plants. Magnesium is contained in chlorophyll and is involved in photosynthesis.

Calcium is the most abundant element of the second group. Being an active metal, calcium occurs in nature in the form of its compounds exclusively. Its mineral calcite $CaCO_3$ is one of the most abundant in the Earth's crust. It occurs sometimes in the form of crystals, but is mainly as limestone, chalk, and marble.

Chalk is mostly soft porous natural material composed of the calcareous remains of marine organisms (Fig. 6.6). Limestone is harder and its granular structure is not apparent. Marble has crystalline, and granular structure; its fracture resembles that of sugar. Limestone is contained in some soils (known as calcareous soils). Sometimes the limestone content in soil is so high that if hydrochloric acid is poured on the ground it 'boils'. (Why?) Gypsum deposits are also abundant. Gypsum is very soft and can be crushed by the pressure of a finger nail. Calcium compounds are contained in plant and

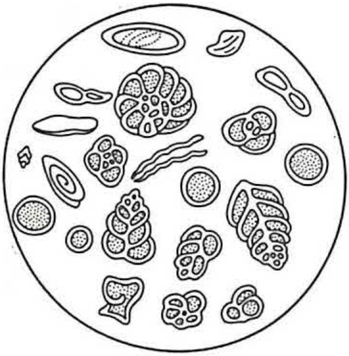


Fig. 6.6 Chalk viewed in a microscope

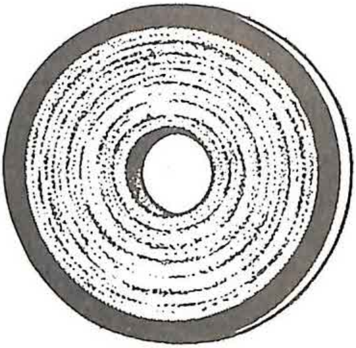


Fig. 6.7 Pipe section of hot water supply system.

The lumen is almost completely closed by scale

animal tissues. The concentration of calcium phosphate in the mineral component of the bones is about 80 per cent.

Calcium compounds are widely used everywhere. Limestone is used to make the construction materials, burnt lime and cement. Chalk is used in the manufacture of rubber and dyes.

Limestone, lime, and lime-containing industrial wastes are widely used in agriculture to decrease acidity of soils and to improve its structural characteristics.

■ Collect materials that in your opinion might contain calcium carbonate and try them with vinegar solution of acetic acid in water). Try also the shell of an egg, a piece of scale from your tea kettle, and tooth cleaning powder.

? △

1. What are the alkaline-earth metals? Why these metals are not used in the manufacture of any articles?
2. What regularities can be established in the change of the chemical properties of metals in the main subgroup of group II with their increasing atomic numbers?
3. What metal in this subgroup has more pronounced, less pronounced metallic character? How does this manifest?
4. Write the ionic equation for the reaction between magnesium nitrate and lime water.

6.8 Hardness of Water and Ways to Remove It

Before natural water is delivered to the water-supply system or into a well, it passes through soil and becomes saturated with soluble salts.

Natural water contains sulphates and bicarbonates of calcium and magnesium, i.e. Ca^{2+} and Mg^{2+} cations and SO_4^{2-} and HCO_3^- anions.

Water containing insignificant amounts of Ca^{2+} and Mg^{2+} ions is called soft, and if these cations are contained in large amounts, water is called hard.

When hard water boils, bicarbonates are decomposed to form insoluble carbonates, e. g.

$$Ca^{2+} + 2HCO_3^- = CaCO_3\downarrow + H_2O + CO_2\uparrow$$

The carbonates precipitate and water hardness decreases. Hardness of water due to the presence of bicarbonates of calcium and magnesium is called *removable* or *temporary*. Hardness due to the presence of other salts of calcium and magnesium, which cannot be removed by boiling, is called *permanent*.

A soft water readily forms lather while a hard water does not. Let us try the soap to hard and soft water. Take a solution of gypsum to imitate hard water. Place a dilute solution of soap into a burette and add it gradually (portion by portion) to hard water, shaking vigorously after adding each new portion. The first portions of soap will be spent to form a flake-like precipitate and no lather will be produced. As soon as precipitation discontinues, the solution begins foaming on shaking.

Soaps are sodium (sometimes potassium) salts of organic acids and their compostion can conventionally be expressed as NaR or KR, where R is the acid residue. Anions R react with calcium or magnesium cations to give insoluble salts CaR_2 and MgR_2. First portions of soap are thus wasted to form these insoluble salts. Using a soap solution we can estimate the total hardness of water, the total content of calcium and magnesium ions in it.

Hardness of water for domestic use should be insignificant. Scale is formed during boiling of hard water. Cooking meat, vegetables, or cereals becomes difficult in hard water. When laundry is made in hard water, insoluble salts, that are formed during washing, precipitate on fibres and destroy them gradually.

If hard water is delivered to the boiler, scale is deposited on the boile's walls to interfere with normal heat exchange. Hence increased consumption of fuel and premature wear of boiler's walls (Fig. 6.7).

In order to decrease water hardness various chemicals are used, which convert calcium and magnesium ions into insoluble salts (normally into carbonates).

Temporary hardness is removed by adding milk of lime:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O$$

Permanent hardness can be removed by adding soda:

$$CaSO_4 + Na_2CO_3 = CaCO_3\downarrow + Na_2SO_4$$

? △

1. What is harder, rain or river water? Why?
2. Why does river water contain bicarbonates of calcium and magnesium?
3. How can water be softened without using any chemicals?
4. Write ionic equations for the reactions by which (a) temporary, and (b) permanent hardness can be removed.

5. Permanent hardness of water containing gypsum cannot be removed by adding calcium hydroxide. Why?

6. Test water from various local sources for hardness.

Aluminium is the subject matter of our next lesson.

1. Take a piece of aluminium foil. Describe the physical properties of aluminium.

2. Try aluminium if it burns in air or melts. To that end cut out a strip of aluminium foil, fix its one end (hold by pincers) and put a lit match to the free end. Observe and describe. (Why does molten aluminium not drip off the strip? Discuss this question at the lesson.)

3. Place pieces of aluminium foil in water, in sal ammoniac, and in vinegar. Observe for a few days and describe the results of observations. Discontinue observations when foil turns into a delicate openwork in one of these solutions. Do not discard it.

6.9 General Characteristics of Elements of the Main Subgroup of Group III

The subgroup comprises boron, aluminium, gallium, indium, and thallium. The outer layers of their atoms have three electrons. If these electrons are given off during formation of compounds, the chemical elements of this subgroup will have the oxidation number 3+.

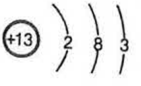
From their position in the periodic system one can expect that the elements of the main subgroup of Group III will have less pronounced metallic properties than the elements of the main subgroup of Group II. Beryllium has the properties of both metals and nonmetals, while boron, which stands to the right of beryllium, would mainly exhibit nonmetallic properties. This is true: boron forms an acid oxide B_2O_3 and the corresponding hydroxide H_3BO_3, boric acid.

Aluminium stands in the third period between the metal calcium and nonmetal silicon. The physical properties of aluminium in the free state are typical of metals, while its chemical properties differ in some respects from that of metals: aluminium can react both with acids and alkalis. Aluminium compounds are amphoteric.

The properties of gallium and indium are very similar to those of aluminium but the nonmetallic character weakens while the metallic properties strengthen from aluminium to indium. Thallium can be a ter- and univalent metal. Compounds of inivalent thallium are similar in their properties to compounds of the alkali metals. This is explained by similarity of dimensions of the Tl^+ ion and the ions of the alkali metals.

6.10 Aluminium

The chemical symbol of aluminium is Al, its atomic number 13, its atomic weight 27, and the structure of atom is



Aluminium is the most abundant element in the third group. This is a silvery-white, light metal, its density is 2.7 g/cm^3. Aluminium melts at a considerably low temperature 659 °C: aluminium foil easily melts in the flame of a burning match.

Aluminium is a good conductor of electricity and heat. Its electrical conductivity is about 2/3 of copper. Aluminium is very ductile and can be drawn into wires and rolled into foil.

During chemical reactions aluminium gives off three electrons from its outer layer and turns into a tripositive ion Al^{3+}. In all its stable compounds, aluminium has the oxidation number 3+.

Aluminium stands near the alkali and alkaline-earth metals in the electrochemical series and must therefore show itself as a chemically active metal. Doesn't it contradict our everyday observations? We use aluminium kettles and pans to boil water and cook food and do not notice appreciable changes in the aluminium utensils. One can get an impression that neither oxygen nor boiling water affect aluminium.

Let us carry out an experiment to explain this apparent contradiction. Fix an aluminium wire in an inclined position in the clamp of a laboratory stand and heat the free end in the flame of a burner. The hot end of the wire suddenly sags. If we look attentively at the hot end, we can see that the aluminium wire is coated with a semitransparent film inside which molten aluminium shines like silver. The molten aluminium forms a drop at the end of the wire. The film is aluminium oxide. When heated in air, aluminium surface is oxidized without burning and aluminium oxide Al_2O_3 is formed:

$$\overbrace{4\,\mathrm{Al} + 3\mathrm{O}}^{12\bar{e}}{}_2 = 2\,\mathrm{Al}_2\mathrm{O}_3 + Q$$

Aluminium combines with oxygen of the air at ordinary temperature as well. A thin but dense film of aluminium oxide is formed on the surface which is impermeable for gases and thus protects the metal from further oxidation.

When the surface of aluminium is damaged, the oxide film is damaged as well but a new film of the oxide is immediately formed. When aluminium dissolves in reagents that do not act upon aluminium oxide, the oxide film separates in the form of fine transparent strips.

The existence of the oxide film on the surface of aluminium can be proved as follows. Place a piece of aluminium in mercury and make several notches by a file under the layer of mercury (in order to prevent the contact of aluminium with air). An alloy of aluminium with mercury, known as amalgam, will be formed in the notches. The oxide film does not stick to the amalgamated surface and separates. Its protective action becomes ineffective and aluminium removed from mercury soon oxidizes at the scratched sites: white fleecy aluminium oxide is formed (Fig. 6.8).

We can now easily explain the passive reaction of aluminium to water. The absence of reaction between aluminium and water is explained by insolubility of the oxide film that protects aluminium surface.

If the film is removed by scratching under mercury, and aluminium is quickly transferred into water, it will react energetically with water to

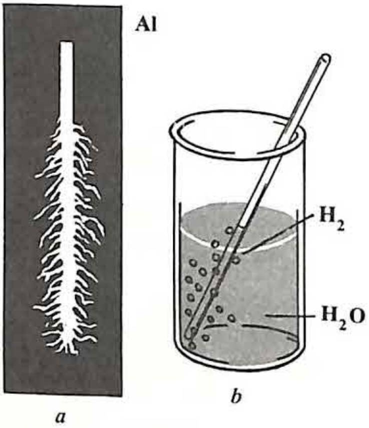


Fig. 6.8 Oxidation of amalgamated aluminium:
a – in air; *b* – in water

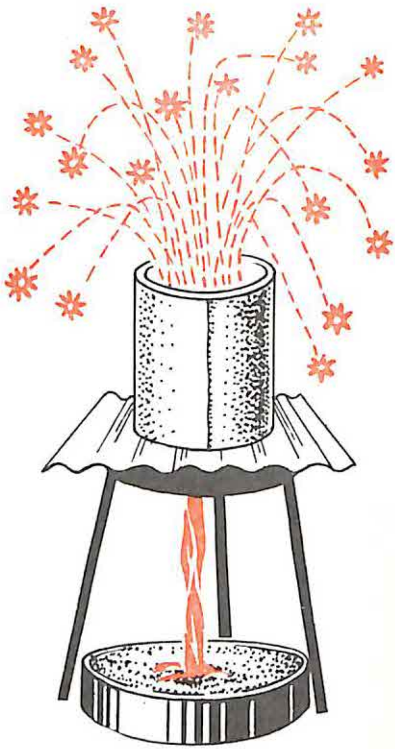


Fig. 6.9 Reduction of iron from its scale by aluminium

displace hydrogen from it:

$$2Al + 6H_2O = 2Al(OH)_3 \downarrow + 3H_2 \uparrow$$

The oxide and hydroxide of aluminium are known to be amphoteric. They dissolve in acids to give access to aluminium metal.

Place aluminium shavings into a test tube containing hydrochloric acid or in a test tube with dilute sulphuric acid. Aluminium dissolves to displace hydrogen from the acid and to form a salt, e. g.:

$$2Al + 6HCl = 2AlCl_3 + 3H_2 \uparrow$$

Aluminium reacts with dilute nitric acid and does not react with concentrated nitric acid at normal temperature. Concentrated nitric acid can therefore be kept in aluminium containers and transported in aluminium tank cars.

When heated, aluminium reacts with most metal oxides, iron scale included. Pure iron and aluminium oxide are obtained in this reaction:

$$8Al + 3Fe_3O_4 = 9Fe + 4Al_2O_3 + 3241\ kJ$$

Make a cup from asbestos and wire, place it on an iron sheet on a tripod, and put a dish with sand under the sheet as shown in Fig. 6.9. Place a mixture of aluminium powder and iron scale into the asbestos cup, insert a magnesium ribbon into the mixture, and light it. The magnesium ribbon acts like a primer that ignites the aluminium-iron scale mixture. The mixture burns splashing around white-hot sparks of burning reduced iron. The reaction is exothermic and a temperature of about 3000 °C develops in the mixture at which both reaction products (iron and aluminium oxide) are melted. When the mixture burns to the bottom to reach the iron sheet, the latter melts, and the molten mass pours down into the sand under the iron sheet. An ingot of smelted iron can be separated from the sand by knocking on the solidified mass with a hammer.

6.11 Uses of Aluminium

Main uses of aluminium (see plate II on page 179) are connected with its light weight, strength, and stability of aluminium alloys to air and water. Transportation mechanisms need this combination of physical and chemical properties. The main consumers of aluminium alloys are therefore aircraft and automobile industries. Substitution of aluminium alloys for steel in cars and aircraft makes their control easier and decreases fuel consumption.

The use of aluminium alloys in construction is due to the same properties. Aluminium alloys successfully substitute for steel, wood, reinforced concrete, and many other building materials especially when local building materials are not available and their transportation from other areas is difficult. For example, corrugated sheets from alluminium alloys were used to build granaries in far-off virgin lands of Kazakhstan.

'Silver' paint, which is widely used in construction and architecture, is a mixture of aluminium powder and mineral oil. It improves the appearance of various structures and also protects them from chemical action of the environment and from heat radiation. Silver paint protects, for example, petroleum products kept in containers from their overheating by the sun rays.

High electrical conductivity of pure aluminium is used in electrical engineering. Conductors are manufactured from aluminium. Though copper is a better conductor of electricity, an aluminium wire, imposing the same resistance as a copper one, will be twice as light. This simplifies the construction of masts from which electric wires are hanged.

Many kitchen utensils are now made of aluminium. Apart from lightness and strength, other valuable properties of aluminium are also utilized here, namely, high heat conductivity, resistance to cold and boiling water, and the absence of hazardous compounds that might be formed by weak organic acids contained in foods on aluminium.

△

1. Write down molecular and electron equations for the reactions characterizing the properties of aluminium.
2. Compare the chemical properties of sodium, calcium and aluminium. Relate the results to the structure of their atoms.
3. Write ionic equations for the reactions between: (a) aluminium

and hydrochloric acid, (b) aluminium and blue vitriol solution. 4. What uses of aluminium do you know?

■

1. Make out a list of aluminium articles that may be found at home, and explain what property of aluminium and its alloys account for each particular use of the household article.
2. Place water in a dish. Make a ball of cramped paper, and place it in water. Now place two nails and pieces of aluminium foil on the paper. (Lubricate one nail with vaseline or vegetable oil.) Observe the changes that may occur in iron and aluminium for a few days. Do not forget to add water from time to time or replenish its loss. Record your observations and the date of each observation. Draw a conclusion concerning comparative chemical stability of aluminium and iron toward the air and water.

6.12 Aluminium Compounds

Aluminium oxide Al_2O_3 is a white solid. It is high-melting (m. p. is above 2 000 °C) and is very hard. Natural aluminium oxide is corundum. It is the hardest natural substance after diamond. Abrasive tools, such as polishing wheels, or bricks, are manufactured from corundum and used for cutting, and polishing of metal and other articles.

The special hardness of corundum is due to the strong mutual attraction between the Al^{3+} and O^{2-} ions that form the lattice. The strength of their mutual attraction depends on their great charges.

Aluminium oxide is not soluble in water, nor does it react with it. Aluminium oxide is amphoteric. It acts as a basic oxide toward acids, i.e. dissolves in acid solutions to form aluminium salts, e.g.

$$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O$$

Write the ionic equation for this reaction without assistance.

Aluminium oxide behaves like an acid oxide with respect to alkalis: it dissolves with formation of salts, aluminates of the alkali metals, e.g.:

$$Al_2O_3 + 2NaOH + H_2O = \underset{\text{sodium aluminate}}{2NaH_2AlO_3}$$

Write the ionic equation for this reaction.

Aluminium hydroxide $Al(OH)_3$ is a white solid insoluble in water. It is obtained by the reaction between aluminium salts and alkalis. If a solution of sodium hydroxide is added drop by drop to a solution of aluminium chloride, a jelly-like precipitate of aluminium hydroxide is formed:

$$AlCl_3 + 3NaOH = Al(OH)_3\downarrow + 3NaCl$$

The net ionic equation for this reaction is

$$Al^{3+} + 3OH^- = Al(OH)_3\downarrow$$

If any acid, for example HCl, is added to aluminium hydroxide, the precipitate disappears: a water-soluble salt of aluminium is formed:

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$$

The ionic equation is

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$$

Aluminium hydroxide exhibits basic properties in this reaction.

If sodium hydroxide solution is added to aluminium hydroxide, a clear solution is also obtained; this is explained by the formation of a water-soluble sodium aluminate:

$$H_3AlO_3 + NaOH = NaH_2AlO_3 + H_2O$$

The ionic equation of this reaction is

$$H_3AlO_3 + OH^- = H_2AlO_3^- + H_2O$$

Aluminium hydroxide exhibits its acid properties in this reaction. It means that aluminium hydroxide can be either acid or alkali depending on the conditions. Aluminium hydroxide is amphoteric.

If an aluminium wire is placed in a hot alkali solution, vigorous liberation of hydrogen soon begins. How can this phenomenon be explained? Metallic aluminium is coated with the film of amphoteric aluminium oxide. It reacts with the alkali to give a water-soluble sodium aluminate and water. Free of its protective oxide coat, aluminium reacts now with water.

Destruction of aluminium in an alkaline medium should be remembered when we use aluminium articles in the home.

Aluminium in nature. Aluminium is the most abundant metal in the Earth's crust. Owing to its high chemical activity it does not occur in the free state in nature. Among natural aluminium compounds there are aluminosilicates, bauxites, corundum, and its variety emery.

Aluminosilicates are salts whose anions contain aluminium and silicon Cations of these salts are the alkali and alkaline-earth metals. Aluminosilicates make the main bulk of the Earth's crust. The widely occurring mineral feldspar is also aluminosilicate.

Bauxite is the main ore of aluminium, whose main component is aluminium hydroxide. Bauxites have formed by decomposition of various rocks (by weathering). The products of decomposition were carried away with water into lakes and seas, where they precipitated near the coastal line.

?

△

1. What substances and in what sequence are formed when sodium hydroxide solution is added to aluminium chloride solution? Write the corresponding reaction equations.
2. Why cannot alkalis be kept in aluminium containers? Write equations for the reactions that may occur.
3. By what reactions can aluminium ions be detected in solution?

7

Metals of the Secondary Subgroups of the Periodic System

7.1

Structure of Atoms of Metals of Secondary Subgroups

We have already studied the metals of the main subgroups of groups I, II, and III. Now we shall study the properties of metals standing in the secondary subgroups. But let us first discuss the structure of the atoms of these elements because it accounts for the specific properties of these metals.

Let us remember how the electron layers of atoms of chemical elements standing in the main subgroups change in the transition from one element to another in short periods. The charge of the atomic nucleus increases one unit because one distinguishing electron is added. The distinguishing electron is added in the first twenty chemical elements (from H to Ca) either to the electrons in the outer layer of the preceding element, or it begins a new outer layer. The electron is added to the outer layer in the transition from magnesium to aluminium or from potassium to calcium, and a new layer is formed in the transition from helium to lithium and from argon to potassium.

The picture is different with metals of the secondary subgroups. The last electron is usually added not to the outer but to the penultimate layer.

Consider by way of illustration the gradual changes occurring in the electron layers in atoms of the fourth period, from scandium to zinc. Scandium (at. No. 21) has 21 electrons (as compared to 20 in calcium). The 21st electron was added to the penultimate layer which now counts 9 electrons. The electron distribution by layers in scandium is as follows: $(+21) - 2 - 8 - 9 - 2$. In titanium (at. No. 22) the penultimate layer contains ten electrons, and that of vanadium (at. No. 23), 11 electrons. Chromium (at. No. 24) should contain 12 electrons in the penultimate layer but one more electron is added to this layer from the outer layer, and the latter now contains only one electron. This arrangement is more advantageous energetically: $(+24) - 2 - 8 - 13 - 1$. As electrons are gradually added the penultimate layer of zinc (at. No. 30) becomes fully occupied with electrons. The electrons are distributed in zinc as follows $(+30) - 2 - 8 - 18 - 2$.

The same mode of filling electrons in the layers is observed in many elements of secondary groups in the Vth, VIth, and VIIth periods. One or two electrons are contained in the outer layer of their atoms.

There are elements in the secondary subgroups whose atoms accommodate each distinguishing electron not in the penaltimate but in the third layer from outside. These elements are metals and they are located in those boxes of the secondary subgroup of group III which belong to periods VI and VII. In the VIth period these are lanthanum and the lanthanides, and in the VIIth period, actinium and the actinides.

? △

1. Draw diagrams of atomic structure of yttrium (at. No. 39) and indium (at. No. 49). Whose structure is characteristic of the metals of the secondary subgroups?
2. Draw diagrams of atomic structure of manganese and bromine. Indicate their similarity and differences.

7.2

Properties of Oxides and Hydroxides of Metals of the Secondary Subgroups and Their Dependence on Oxidation Number

In contrast to metals of the main subgroup, elements of the secondary subgroups can donate various number of electrons from the outer and penultimate layers of their atoms, and can therefore exhibit more than one oxidation number in chemical reactions. Titanium, the metal of the secondary subgroup of group IV, has three oxidation numbers: 2+, 3+, and 4+, while vanadium, that comes next to titanium in the period, from 2+ to 5+, chromium 2+, 3+, and 6+, manganese from 2+ to 7+. Each metal in the secondary subgroups can therefore form several oxides and the corresponding hydroxides, which differ in their properties and composition.

Consider certain regularities in the change of properties of compound of the metals standing in the secondary subgroups. Use chromium compounds as an example.

Chromium in the free state is a metal resembling steel in appearance. Like all metals, in which the penultimate layer is being filled with electrons, it differs from the discussed metals by its special hardness and refractoriness. Chromium is the hardest metal; it leaves scratches on glass. Chromium oxidizes in air to form a thin film on its surface which protects the metal from further oxidation. Chromium is therefore used for electroplating steel to prevent it from corrosion and mechanical abrasion. When alloyed with iron, chromium gives it its hardness. Chrome steels contain from 12 to 14 per cent by weight of chromium. Chrome-nickel stainless steel contains about 18 per cent of chromium.

Stainless steel is widely used in chemical, food, space industries, etc. In the home we use chrome-plated spoons and forks, and other household objects.

Chromium originates from the Greek word *chroma* which means colour, because all chromium compounds are coloured bright.

In chemical reactions, the chromium atom can give off not only its single electron from the outer layer but also to 5 electrons from the penultimate layer. In these reactions chromium exhibits its higher oxidation number 6+. But like all other elements in which the electrons are added into the penultimate layer, chromium has several oxidation numbers, i.e. it can also have lower oxidations numbers, viz. 2+ and 3+.

When chromium is dissolved in acids, it forms salts in which the oxidation number of chromium is 2+

$$\underset{}{Cr^0} + 2H^{1+}Cl^{1-} = \underset{\text{chromium (II) chloride}}{Cr^{2+}Cl_2^{1-}} + H_2^0 \uparrow$$

The net ionic equation is

$$Cr^0 + 2H^+ = Cr^{2+} + H_2 \uparrow$$

Because of the Cr^{2+} ion, the obtained solution is blue. When alkali is added to it, yellow-brown chromium(II) hydroxide precipitates:

$$CrCl_2 + 2NaOH = Cr(OH)_2 \downarrow + 2NaCl$$

$$Cr^{2+} + 2OH^- = Cr(OH)_2 \downarrow$$

Chromium(II) hydroxide is a base and the corresponding oxide of chromium(II) CrO is a basic oxide.

Compounds in which the oxidation number of chromium is 2+ can be oxidized to compounds in which the oxidation number of chromium is 3+. The following reaction occurs in an acidified solution containing dissolved oxygen:

$$\underset{\text{blue solution}}{4CrCl_2} + 4HCl + O_2 \rightarrow \underset{\text{green solution}}{4CrCl_3} + 2H_2O$$

Chromium(III) oxide Cr_2O_3 is green. It crystallizes in the same lattice as aluminium oxide. Like aluminium oxide, chromic oxide is hard, high-melting, and is also used as an abrasive material. The finest powder of chromic oxide is used to polish glass and articles from hard materials. Chromium(III) oxide is also used as a fast mineral dye.

In natural aluminium oxide crystals part of aluminium ions are replaced by the Cr^{3+} ions which colour the crystal red. These crystals are called ruby and are valued as gem stones. Miniature bearings for clockwork are made of rubies. Artificial rubies are obtained by fusing aluminium oxide with a small quantity of chromium(III) oxide.

Chromic oxide (like aluminium oxide) is insoluble in water, it does not react with water, and is amphoteric.

Chromium(III) hydroxide $Cr(OH)_3$ precipitates as a green gelatinous substance when alkali solution is added to a solution of a chromium(III) salt:

$$CrCl_3 + 3NaOH = Cr(OH)_3 \downarrow + 3NaCl$$

Write the ionic equation for this reaction.

Like aluminium hydroxide, chromic hydroxide is amphoteric. It dissolves in acid solutions to form the initial greenish violet salt of chromium(III) (the colour of the hydrated Cr^{3+} ions). In alkali solutions it forms green chromites, the colour of which is due to the presence of the ions $H_2CrO_3^-$:

$$Cr(OH)_3 + 3HCl = CrCl_3 + 3H_2O$$
$$Cr(OH)_3 + NaOH = NaH_2CrO_3 + H_2O$$

Chromium(III) salts are similar to aluminium salts in their composition, crystal lattice, and solubility.

Chromium(VI) oxide CrO_3 is an acid oxide. It combines with water to form two acids, viz. chromic acid H_2CrO_4 and dichromic acid $H_2Cr_2O_7$. Salts of the former acid, e. g. Na_2CrO_4 are yellow (the colour of the CrO_4^{2-} ions). They are called chromates. Salts of the other acid, e. g. $Na_2Cr_2O_7$ are orange (the colour of the $Cr_2O_7^{2-}$ ions). These are called dichromates.

Hydroxides of chromium (VI) are thus acids themselves. When chromium exhibits its oxidation number 6+, its compounds are similar in their properties to compounds of sulphur with the same oxidation number.

Like sulphur (VI) oxide and sulphuric acid, chromium (VI) oxide and chromic acid are oxidants. Ammonia, for example, ignites when comes in contact with chromium (VI) oxide:

$$2Cr^{6+}O_3 + 2N^{3-}H_3 = Cr_2^{3+}O_3 + N_2^0 + 3H_2O$$

The oxidizing properties of chromium salts are most pronounced in an acid medium. When any acid is added to a salt dichromate, the orange colour of the solution does not change. But if any reductant, e. g. a sulphite, is added to the solution, the orange colour which is characteristic of the $Cr_2O_7^{2-}$ ions, changes to greenish-violet, characteristic of the hydrated ions of tervalent chromium:

$$Na_2Cr_2^{6+}O_7 + 3Na_2S^{4+}O_3 + 4H_2SO_4 = Cr_2^{3+}(S^{6+}O_4)_3 + 4Na_2S^{6+}O_4 + $$
$$+ 4H_2O$$

The composition and properties of chromium compounds are compared in Table 7.1.

Table 7.1

Chromium Compounds

Oxidation number	Formula of oxides	Properties of oxides	Formula of hydroxides	Properties of hydroxides
Cr^{2+}	CrO	Basic oxide, reductant	$Cr(OH)_2$	Base, reductant
Cr^{3+}	Cr_2O_3	Amphoteric	$Cr(OH)_3$	Amphoteric
Cr^{6+}	CrO_3	Acid oxide, oxidant	H_2CrO_4	Acid, oxidant

The following regularities can be formulated. As the oxidation number of the metal of the secondary subgroup increases, the properties of its oxides and hydroxides change in the same way as they do in elements of one and the same period with their increasing oxidation number: the basic properties change through amphoteric to acid.

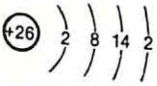
Compounds of elements with lower oxidation numbers have reducing, and compounds with the higher oxidation number, oxidizing properties.

△

1. Compare the properties of chromium(III) compounds with that of aluminium, chromium or sulphur(VI) compounds.
2. What properties (oxidizing or reducing) are characteristic of chromium(III) oxide and chromium(III) hydroxide?
3. Write formulas of the lower oxide and the corresponding hydroxide of manganese. Describe the chemical properties of these compounds.
4. Describe the properties of the higher manganese oxide and the corresponding hydroxide. Write the formulas of these compounds and equations which involve these substances.

7.3 Iron

The chemical symbol of iron is Fe, its atomic number 26, its atomic weight 56, and the atomic structure



In addition to two electrons of the outer layer, electrons of the penultimate layer can also be eliminated from the iron atom in chemical reactions. The oxidation number of iron in its compounds is usually 2+ and 3+.

Iron is a silvery-white metal; it is very ductile, readily malleable, and can be drawn into wire. The property of iron that distinguishes it from other metals is its magnetism: it is attracted by a magnet and can become a magnet itself if electric current is passed through wire coiled round an iron core.

If an iron wire is heated by passing electric current of increasing density, the wire first sags because of thermal expansion, but as the temperature rises to 910°C, the wire is suddenly stretched, i.e. iron shrinks. The atoms of iron are rearranged in the crystal lattice at this temperature. The lattice becomes compacted and common iron (α-iron) turns into another allotrope of iron, γ-iron. In contrast to α-iron, the gamma modification is nonmagnetic and can be carbonized, i.e. carbon atoms can dissolve in iron to give a solid solution of carbon in iron, in which the carbon atoms enter the interestices between the iron atoms in the crystal. Gamma iron can hold not more than 2 per cent of carbon in the form of solid solution.

Iron melts at temperatures above 1 500°C to turn into a mobile liquid. Liquid iron absorbs carbon easier than solid gamma iron (to 4 per cent). When iron alloys solidify, dissolved carbon can crystallize out as graphite or cementite (ferrous carbide) Fe_3C, or remain in solid solution.

Iron forms several compounds:

FeO	$Fe(OH)_2$	$FeCl_2$, $FeSO_4$, etc.
Iron (II) oxide	iron (II) hydroxide	salts of iron (II)
Fe_2O_3	$Fe(OH)_3$	$FeCl_3$, $Fe_2(SO_4)_3$, etc.
Iron (III) oxide	iron (III) hydroxide	salts of iron (III)

Apart from FeO and Fe_2O_3, iron can form an intermediate oxide in which a part of iron is present in divalent and a part, in tervalent state:

$$Fe_3O_4 = Fe^{2+}Fe_2^{3+}O_4^{2-}$$

Iron burns in oxygen with bright splashes which are white-hot particles of iron scale Fe_3O_4. When heated in air, iron surface oxidizes to form a crust of iron scale which is separated from the metal when it is hammered. Sparks that are formed during sharpening of iron tools or during casting molten iron are white-hot particles of the same iron scale. The same reaction occurs in all these cases:

$$3Fe + 2O_2 = Fe_3O_4 + Q$$

Consider now the reaction of iron with water and oxygen at normal temperature. Place three iron nails into separate test tubes, one of which contains dry oxygen, the other water (preliminarily boiled to remove dissolved oxygen), and the third oxygen (the test tube is overturned into a dish containing water). No apparent changes occur in the former two test tubes while the iron rusts in the third test tube and the liquid level in it rises. This indicates that oxygen is consumed to oxidize iron. Yellow-brown rust is formed, which is mainly ferric hydroxide:

$$4Fe + 6H_2O + 3O_2 = 4Fe(OH)_3$$

Rust attacks not only the part of the nail that is immersed in water, but separate spots appear on the dry end as well.

One can conclude that neither dry oxygen, nor water in the absence of oxygen affect iron. But in moist air and in water containing dissolved oxygen, iron rusts and is covered with a loose easily detachable crust. It is permeable for gas and vapour and cannot thus protect the metal from further corrosion. As soon as a rusted spot appears on an iron article, it adsorbs moisture from the air and accelerates further corrosion. Once iron is attached at one point, rusting spreads over the rest of the iron.

Iron comes before hydrogen in the electrochemical series. It is therefore dissolved in dilute sulphuric and hydrochloric acids to displace hydrogen from them and to form the corresponding salt, in which iron is divalent:

$$Fe + H_2SO_4 = \underset{\substack{\text{iron (II)} \\ \text{sulphate}}}{FeSO_4} + H_2\uparrow$$

The net ionic equation is

$$Fe^0 + 2H^+ = Fe^{2+} + H_2\uparrow$$

But concentrated sulphuric and nitric acids do not react with iron at normal temperature because dense films of iron compounds, insoluble in these acids, are formed on the iron surface.

Iron displaces copper and other metals, that come after iron in the electrochemical series, from aqueous solutions of their salts:

$$Fe + CuSO_4 = Cu + FeSO_4$$

The net ionic equation is

$$Fe + Cu^{2+} = Fe^{2+} + Cu$$

As during dissolution in acids, iron is oxidized to 2+.

?
△

1. Describe (a) physical and (b) chemical properties of iron.
2. Write equations for the reactions of iron with solutions of (a) hydrobromic acid, and (b) silver nitrate.
3. Blue vitriol solution is used to treat walls and ceiling before white-washing them. Can blue vitriol be kept in iron pails?

7.4

Iron Compounds

Iron(II) salts are slightly green in solution, the colour being due to the hydrated Fe^{2+} ions. When an alkali solution is added to an iron(II) salt, e.g. ferrous chloride, white flakes of ferrous hydroxide precipitate:

$$FeCl_2 + 2NaOH = Fe(OH)_2\downarrow + 2NaCl$$

Write down the net ionic equation by yourselves.

The precipitate immediately turns green on exposure to air and then turns brown because the ferrous hydroxide oxidizes into ferric hydroxide:

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3\downarrow$$

Ferrous hydroxide does not dissolve in excess alkali, but it readily dissolves in acids to turn into iron(II) salts:

$$Fe(OH)_2 + 2HCl = FeCl_2 + 2H_2O$$

Write the net ionic equation.

Ferrous hydroxide is therefore a base. Solutions of iron(III) salts, e.g. $FeCl_3$ are yellow. When an alkali is added to these salts a yellow-brown ferric hydroxide precipitates:

$$FeCl_3 + 3NaOH = Fe(OH)_3\downarrow + 3NaCl$$

Write down the net ionic equation.

Ferric hydroxide dissolves in acids to yield iron(III) salts:

$$Fe(OH)_3 + 3HCl = FeCl_3 + 3H_2O$$

Write the net ionic equation.

Ferric hydroxide is thus a base, like ferrous hydroxide. But ferric hydroxide is a weaker base, and solutions of iron(II) salts therefore hydrolyze weakly while those of iron(III) hydrolyze so strongly that hydrolysis continues until colloidal particles of ferric hydroxide are formed (remember the experiment in which a colloidal solution of iron(III) hydroxide was obtained). The yellow colour of ferric salts is not due to the Fe^{3+} ions but to colloidal particles of iron(III) hydroxide. $Fe(OH)_3$ dissolves in concentrated alkali solutions like $Al(OH)_3$ to form the ferrites MeH_2FeO_3 (like MeH_2AlO_3).

The increase in the charge of the iron ions from 2+ to 3+ strengthens the bonds between its ions and hydroxide ions.

Green vitriol $FeSO_4 \cdot 7H_2O$ is the most common salt of iron. It is used in the manufacture of dyes and to impregnate wood to prevent its decay.

Iron is the second most abundant metal after aluminium. Its most important ores are haematite Fe_2O_3 and magnetite Fe_3O_4. The world largest deposits of iron ore are found in the Soviet Union in the Urals, near the city of Kursk and Krivoy Rog. Iron is a component of plant and animal tissues. It is contained in haemoglobin of blood which is responsible for the oxygen transport from the lungs to other organs and tissues. Although iron is not contained in chlorophyll itself, it is necessary for the production of this substance in plants. Plants growing in iron-deficient soils stop producing chlorophyll and lose their green colour.

?
△

1. How can salts of iron(II) and iron(III) be differentiated if both are soluble in water?
2. Describe the properties of iron hydroxides.
3. Write the equations for reactions by which the following conversions can be realized:

$$Fe_2O_3 \rightarrow Fe \rightarrow FeCl_2 \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow Fe_2O_3$$

7.5

Uses of Iron

Iron is mainly used in practice as its alloys with carbon and other elements. The modern iron-and-steel industry produces iron alloys of various composition. The main alloys of iron are cast (pig) iron and steel.

Cast iron is brittle like glass, while steel is ductile: it can be forged, rolled, drawn, and pressed into various shapes. The difference in the mechanical properties of cast iron and steel is mainly due to the carbon content: the concentration of carbon in cast iron is over 2 per cent and in steels below 2 per cent by weight.

Cast iron contains more carbon than it can bind after solidification, and the excess carbon separates from solidified iron as graphite flakes (Fig. 7.1). The fine lines in the figure are flakes of graphite cut along and across their axes. When cast iron is struck it falls into pieces along the graphite flakes as if they were cracks. Dull grey graphite can be found in the cast iron fracture.

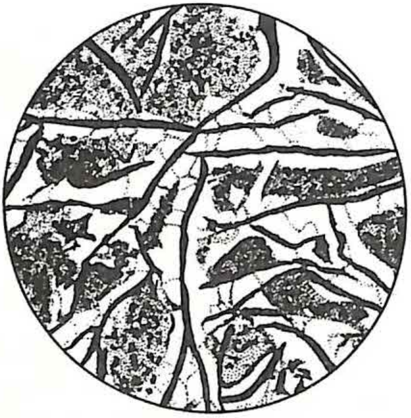


Fig. 7.1 Gray iron (a microscopic view)

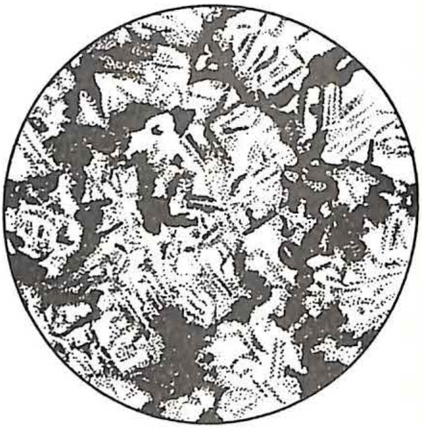


Fig. 7.2 Super-strength pig iron (a microscopic view)

Cast iron is used to make bed plates of various machines and lathes, to manufacture flywheels, slabs, and tubes.

If small amounts of magnesium are added to the molten iron before casting it into molds, the graphite separates out as ball-like inclusions (Fig. 7.2). High-strength cast iron is thus produced and has none of the brittleness of grey iron. Heavy-duty parts for various machines, such as crank-shafts of marine engines, are produced from this metal.

Properties of alloys can thus be varied by altering the shape, size, and arrangement of crystals of the alloy components. This process is known as *modification* and the additives that cause such modification are called *inoculants*.

Mechanical properties of alloys can be improved without inoculants by forging. This process also changes the size and arrangement of crystals in the alloy.

Steel. Steels contain less than 2 per cent of carbon, i.e. the amount that can be held by gamma iron in the solid solution. Graphite does not therefore separate when the molten steel solidifies, instead a saturated solution of carbon in gamma iron is first obtained. Other types of steel arise depending on the speed at which the alloy is cooled. If the alloy cools to room temperature gradually, gamma iron turns into alpha iron, but since carbon is practically insoluble in alpha iron, the solid solution separates into carbon-free iron and cementite. If the molten alloy is cooled suddenly, gamma iron converts into alpha iron but only partially, while carbon does not separate from the crystals. Supersaturated solid solution of carbon in alpha iron is thus obtained (steel hardening). Thus we have

$$\begin{tikzcd}
\text{Melt} \arrow[r] & \begin{array}{c}\text{solid solution of}\\ \text{C in } \gamma\text{-Fe}\end{array} \arrow[r, "\text{rapid cooling}"] \arrow[dr, "\text{slow cooling}"'] & \begin{array}{c}\text{solid solution of C in } \alpha\text{-Fe}\\ \text{(hardened steel)}\end{array} \\
 & & \begin{array}{c}\alpha\text{-Fe} + Fe_3C\\ \text{(tempered steel)}\end{array}
\end{tikzcd}$$

Carbon atoms that remain in iron crystals give the specific properties to hardened steel: hardness, resilience, and also brittleness. To decrease the brittleness, an article is tempered. It is heated again to moderately high temperatures to cause partial decomposition of the solid solution into carbon-free iron and cementite. The hardness of the tempered steel decreases insignificantly, but the brittleness is removed.

The hardening and tempering of steel illustrates another method by which the properties of alloys can be modified without altering their composition. This method is thermal treatment.

The properties of hardened steel depend on the percentage of carbon: the higher the carbon content, the harder the steel. Iron-and-steel industry produces various steels, among which are soft, moderately-hard steels, and high-speed steels. Soft and moderately-hard steels are used in the manufacture of car bodies, household refrigerators, washing machines, corrugated steel, etc., while high-speed steels are used in the manufacture of cutting tools.

Alloy steel. In order to provide specific properties in steels, other elements are added to them. These are called *alloying metals* and steels produced *alloy steels.*

Cutting tools made of ordinary steel do not stand up to high temperatures that develop during high-speed drilling or metal cutting; the steel softens and the tools are quickly dulled. In order to retain carbon in the steel in the solid solution at high temperatures, steel is alloyed with tungsten or chromium. The alloy steel remains hard at high temperatures and is called high-speed steel.

?
△

1. Describe the composition of (a) cast iron and (b) steel. Relate their properties to their composition, and their uses to their properties.
2. What conversions take place in steel during (a) hardening, (b) tempering?
3. How can the properties of alloys be changed without altering their composition?
4. What are alloy steels and high-speed steels?
5*. A small diamond was alloyed with iron. What products were formed? How was the chemical nature of diamond disclosed by the experiment?
6*. Three nails of the same sort of steel were driven into a wooden board. The first was bent by the hammer, the second broke, while the third was driven into the wood. What thermal treatment had been given to each nail?

7.6

Metal Extraction

We have studied the general properties of metals, and got a close acquaintance with some of them, e. g. sodium, potassium, calcium, magnesium, aluminium, chromium, and iron. Let us now discuss methods by which these metals and their alloys are obtained in industry.

The science of industrial extraction of metals is called *metallurgy*. Metallurgy includes the industrial extraction of metals and is subdivided into ferrous and nonferrous metallurgy. Nonferrous metals are further subdivided, according to their properties into light, heavy, noble, and rare metals, etc. Titanium, aluminium, magnesium, the alkali, and alkaline-earth metals are light metals. Copper, lead, nickel, zinc, and tin are heavy metals. Gold, silver, platinum, and the platinum metals are the noble metal.

From what are metals and their alloys extracted?

Accumulations of chemical elements in the form of simple substances or compounds, from which it is reasonable (economically justifiable with the modern status of technology) to recover metals, fuel, chemical products, building and other materials, are called *deposits* (fields). Metals are accumulated in ore deposits. The extraction of minerals from their deposits is done by the mining industry.

Like other minerals, metal ores often contain substances that have no practical value and only interfere with the recovery of metals from the ore. Metal-rich ores are gradually being exhausted and we have to handle raw materials in which the content of valuable substances is low. Iron-poor ores must therefore be first concentrated, i.e. the gangue should be partly removed.

The most important stage of the extraction process is obtaining metal or its alloy from its compounds by chemical methods. This stage is preceded by crushing large pieces of ore or sintering dust particles into larger aggregations. The final stage of the metallurgical process is the pressure treatment of the obtained metal, its casting, thermal treatment, etc.

Metallurgy studies all stages of metal smelting, the process by which metals are obtained. Metallurgy cannot therefore do without chemistry, physics, mineralogy, geology, and other sciences.

Steels are now mostly used in heavy engineering. Over 90 per cent of all the alloys produced is steel. The importance of manganese, chromium, nickel, cobalt, vanadium, molybdenum, tungsten and other alloying elements, that are added to steels, has significantly grown during the 20th century.

Copper and aluminium are the two most important nonferrous metals. The world production of copper is still increasing. This is explained by the high electrical and heat conductivity, strength, stability to corrosion, and good foundry properties. This metal is indispensable in the manufacture of various electrical equipment. About 50 per cent of the total output of copper is spent for these purposes. Copper alloys are used as construction materials in the chemical industry, in the manufacture of precision instruments, and in the automobile industry. However, copper is still expensive and its output does not satisfy the growing demand. For these reasons aluminium and other metals are used instead of copper.

The rapid development of the aluminium industry is due in the first instance to the advantageous combination of its lightness and its strength in alloys, its stability to corrosion, and its good foundry properties.

The abundance of aluminium in nature, development of new and efficient methods of extracting it from its ores account for its wide use. Aluminium is actually the cheapest nonferrous metal.

Magnesium and titanium are the two other important light metals. Magnesium is alloyed with aluminium to give very light but very strong alloys. Magnesium alloys are characterized by their high resistance to corrosion and refractoriness. They are used as construction materials for aircraft and in electronic industry.

Light titanium alloys remain hard at higher temperatures than aluminium and magnesium alloys. They are therefore used to make jet engines. The high corrosion resistance of titanium alloys accounts for their wide use in the manufacture of chemical apparatus and equipment.

Beryllium, zirconium, niobium, cadmium, lithium and some other metals are used in new branches of science and technology, viz. the nuclear, electronic, and space industries.

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△

1. What mineral deposits do you know about in your region? Are there any metal ore deposits among them?
2. What natural sciences underlie metallurgy? Explain your answer.
3. What is the subject matter of the science of metallurgy?
4. Consult reference tables and compare densities of light and heavy nonferrous metals.
5. What alloy steels and which household articles made of these steels do you know?
6. Compare the chemical, technical, and economic data on light metals and their uses. Make out a table.

7.7

Industrial Extraction of Metals

The modern metallurgical industry produces a great number of products including about 75 metals and many thousands of their alloys. The methods by which these products are obtained are numerous and quite varied. Metallurgy faces two major problems: the reduction of metals from their oxides or other compounds, and the separation of the metal from other substances that are formed simultaneously. Thus, for example, in a blast furnace process, iron is reduced from its oxides and cast iron is separated from slag.

The process by which the metal is recovered from its ore often comprises dozens of separate operations, both mechanical and chemical, including the concentration of ores and the purification of the final metal. How is the main process, the reduction of the metal, realized?

Coke and carbon(II) oxide are used in industry to reduce iron and many nonferrous metals such as zinc, lead, etc. The reduction occurs at high temperatures and is sometimes attended by the dissolution of carbon in the metal and the formation of carbides. For example, carbon and the formed iron carbide Fe_3C, cementite, dissolve in the reduced iron. Carbon reduces manganese, chromium, vanadium, and some other metals in a similar way.

If an alloy containing a small percentage of carbon is required, other metals are often used as reductants. Chromium, for example is obtained by reducing chromium(III) oxide with aluminium:

$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr + Q$$

The reaction begins after preliminary heating of powdered chromium(III) oxide and aluminium. It proceeds with liberation of large amounts of heat which is sufficient to melt chromium. Cheaper silicon can be used instead of aluminium for the purpose.

Reduction of metals from their compounds by other metals or silicon is called *metallothermy*.

Metallothermic processes are widely used. Manganese, titanium, and some other metals are produced by metallothermy. Together with aluminium and silicon, magnesium and sodium are also used as reductants.

Reduction with aluminium is called *aluminothermy*.

Highly chemically active metals form very stable compounds with oxygen and other elements. Reduction of their oxides by carbon is either difficult or impossible because of the formation of carbides. It is not always possible or commercially worthwhile to obtain these metals by metallothermy, and electrolysis is therefore used instead.

The electrochemical method of preparing metals is widely used in industry. Electrolysis is used to obtain the alkali and alkaline-earth metals, aluminium, magnesium, and beryllium. Electrolytes should not contain hydrogen ions because during the electrolysis of aqueous solutions of salts of these metals it is not the metal but hydrogen that is liberated at the cathode (remember the electrolysis of aqueous solution of potassium iodide). Neither should the electrolyte contain ions of those metals which can be liberated at the cathode during the electrolysis and thus contaminate the product. The purity of electrolyzed substances is therefore essential and purification of substances for the electrolysis is often the most complicated process in the chain of operations involved in the extraction of metals from their ores.

Electrochemistry is used to purify (*refine*) metals obtained by other methods. In order to purify, say, copper from nickel and iron, anodes made of impure copper are placed in a bath containing sulphuric acid and copper(II) sulphate. As an electric current passes through the electrolyte, pure copper is deposited at the cathode (a copper plate).

We have now discussed the main methods by which metals are reduced in industry. Reduction by carbon or metals at high temperatures are known as *pyrometallurgical processes*. The dissolution of important ore components and isolation of pure products by electrolysis is called a *hydrometallurgical process*.

?
△

1. Write equations for metal reductions by all methods you know.
2. What are the technical and economic advantages and disadvantages of metallothermy compared with direct reduction by coke?
3. What is the main requirement for the composition of the electrolyte intended for obtaining a metal by electrolysis?
4. Electrochemical methods of obtaining metals were known early in

the 19th century. Nevertheless they came in wide use only in the 20th century. Explain this paradox.

7.8 Production of Cast Iron

When iron is reduced in a blast furnace, cast iron is formed, but the heavy engineering industry needs steel. The main bulk of cast iron is therefore converted into steel. The production of steel is a two-step process.

Let us consider the chemical reactions by which cast iron is produced from iron ore.

When iron (III) oxide is reduced, a mixture of iron (II) and iron (III) oxides is first obtained, which is then reduced to iron(II) oxide and finally to pure iron

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$$

Carbon monoxide is used as the reducing agent

$$3Fe_2O_3 + CO \rightleftarrows 2Fe_3O_4 + CO_2 + Q,$$

$$Fe_3O_4 + CO \rightleftarrows 3FeO + CO_2 - Q,$$

$$FeO + CO \rightleftarrows Fe + CO_2 + Q$$

Carbon monoxide is formed in the blast furnace from coke. Coke burns to give carbon dioxide:

$$C + O_2 = CO_2 + Q$$

which reacts with hot coke to yield carbon monoxide:

$$C + CO_2 \rightleftarrows 2CO - Q$$

Iron oxides react also with coke but since the area upon which iron oxide contacts with the solid reductant is much smaller than the contact area between oxides and gas, carbon monoxide plays the main role in the reduction of iron oxides.

Iron partly converts into the carbide at high temperatures

$$3Fe + 2CO = Fe_3C + CO_2 + Q$$

Iron carbide and carbon dissolve in iron to give a relatively low-melting alloy (the melting point of the alloy containing 4.3 per cent of carbon is 1 140 °C, while that of pure iron 1 540 °C).

What happens to impurities contained in iron ore and coke?

Silicon, manganese, phosphorus, and sulphur are partly reduced from their oxides to dissolve in or react with iron. *Liquid iron*, which is an alloy of iron, carbon, silicon, manganese, phosphorus, and sulphur is thus obtained.

Oxides of calcium, magnesium, and aluminium are not reduced in these conditions; nor do they melt. They react with each other to form low-melting silicates, aluminates, aluminosilicates $CaO \cdot SiO_2$, $(CaO)_2 \cdot SiO_2$,

$CaO \cdot Al_2O_3$, $(CaO)_2 \cdot Al_2O_3 \cdot SiO_2$. Most of the sulphur turns into calcium sulphide. These compounds do not dissolve in the liquid iron and form *slag*. A flux such as lime (or limestone) which decomposes in the blast furnace to form lime is also added to the ore to obtain low-melting slags. The temperature at which slag begins to form is about 1 000 °C.

Let us discuss the conditions ensuring high rates of the mentioned reactions so that the efficiency of the blast furnace is high.

The rate of chemical reactions is increased by increasing the concentration of the reactants, the surface area upon which the reactants contact each other, and by raising the temperature.

How can the concentration of iron oxides be increased?

Iron ores are usually concentrated by separating the iron-containing material from the gangue (tails). In order to increase the area upon which the reactants contact one another, the ore, coke, and flux should be crushed. It is desirable that all the lumps should be about the same size because this promotes uniform reactions. Fine-grain concentrated ores, small fragments and dust that are inevitably produced during crushing large lumps of ore, have to be preliminarily sintered into larger aggregations. To that end they are mixed with coal which is burned to provide the necessary sintering temperature. This process is called *agglomeration*. Limestone is added to the sintered mixture and when it is heated, it converts into lime while the gangue is partially slagged. *Fluxed sinter* is thus obtained. The use of fluxed sinter saves expensive coke and increases the efficiency of the blast furnace. (Can you explain why?)

In order to increase the concentration of carbon monoxide, the air delivered into the blast furnace is enriched with oxygen. The concentration of nitrogen in the resultant gaseous mixture is thus decreased and the rate at which coke burns increases, and the concentration of carbon monoxide also increases.

Concentrations of the reactants are increased by adding natural gas containing methane. Methane burns, viz.

$$CH_4 + 2O_2 = CO_2 + 2H_2O + Q$$

and carbon dioxide and water vapour react with hot coke

$$CO_2 + C \rightleftarrows 2CO - Q$$

$$H_2O + C \rightleftarrows H_2 + CO - Q$$

Hence the blast-furnace gas becomes enriched with reducing agents.

Owing to the use of oxygen and natural gas, the rate of the reaction and efficiency of a blast furnace are increased, and so expensive coke is saved.

What are the optimum temperature conditions?

We know that the rate of a chemical reaction depends on temperature, and hence each of the reactions occurring in the blast furnace should be carried out at as high temperature as possible, in accordance with special characteristics of this or that reaction. This is accomplished by preheating the air blown in to 1 300 °C and enriching it with oxygen.

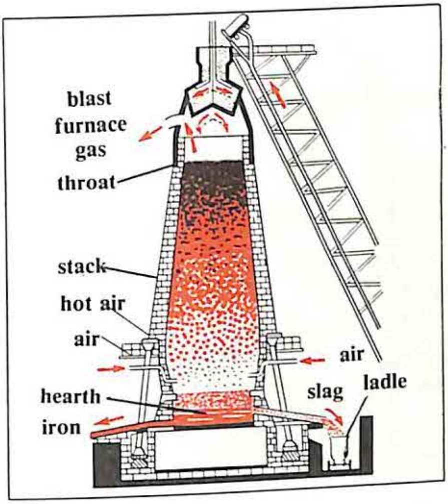

Fig. 7.3 Blast furnace

The heat of exothermic reactions is utilized by heat exchange: hot gas flows from the bottom to the top through liquid cast iron and slag and up through other materials which come in a countercurrent flow (from the top to the bottom). The temperature of the row materials gradually increases and optimum conditions are provided for the reduction and formation of cast iron and slag, and for the formation of carbon monoxide in the lower part of the blast furnace. Iron begins to be reduced from its oxides at about 300 °C. The temperature of the blast furnace gas at the outlet of the furnace is only about 100 °C, the heat thus being utilized quite efficiently. Much carbon monoxide is contained in the blast furnace gas and it is used to preheat air.

A blast furnace is a continuous process apparatus. It is designed to ensure a uniform distribution of gases both across its vertical and horizontal sections, and to provide for continuous washing of the down-flowing charge.

The materials are charged into the furnace by portions or by a belt conveyer as shown in plate III on page 180. The loading device is designed so that hot gas cannot escape into atmosphere when new portions of materials are added. The raw materials are first delivered into the upper hopper from which they are discharged into the lower hopper when the top bell is lowered; the materials are discharged from the lower chamber into the bosh (the combustion zone) when the lower bell is opened. The top bell is closed at this moment and the discharge of hot gas into atmosphere is thus prevented.

Preheated air is blown into the upper part of the hearth through special openings (tuyeres), and the combustion of coke is thus intensified to form carbon monoxide (Fig. 7.3). The blown-in air is preheated by burning combustible products of the blast furnace gas in the apparatus known as the air heating plant. These are high towers lined on the inside with refractory material and packed with special bricks (Fig. 7.4). Blast furnace gas and air are delivered into the combustion chamber where the gas burns. The hot gas

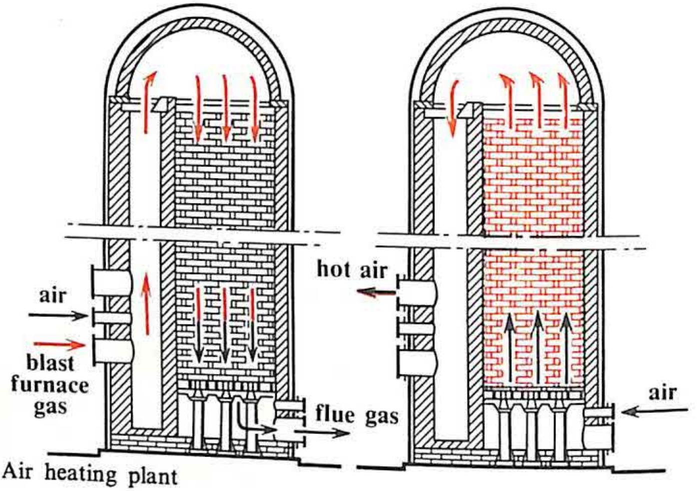

Fig. 7.4 Air heating plant

formed gives off its heat to the packing. As soon as the packing is heated to high temperatures, the delivery of blast furnace gas and air is discontinued and air is now passed in the opposite direction. When the packing is cooled, the air heater is again switched over to heat the packing. In order to ensure a continuous flow of hot air into the blast furnace, each furnace is provided with at least two air heating plants (see plate III).

All the operations to prepare the charge, its weighing and loading into the furnace, and also the periodic discharge of slag and cast iron, etc. are mechanized.

There are some very large blast furnaces in operation in the Soviet Union and their useful volume (i.e. the volume occupied by the charge and molten products) can be as much as 5000 m^3. Such a furnace can give over 4 million tons of cast iron per year.

In order to run such a big blast furnace, reliable information concerning the composition, volume and weight of gases and solids, temperatures, pressures, etc., must be available throughout the process. It can be obtained by numerous automatic devices whose readings are delivered to the central control board.

Many indices characterize the efficiency of operation of a blast furnace, the main of which are the utilization coefficient of the useful volume of the furnace (number of cubic metres of the furnace volume per ton of cast iron per day) and the specific consumption of coke.

?

1. Oxides of what elements cannot be reduced in a blast furnace and why?

△

2. By which reactions are carbon oxides formed in a blast furnace?
3. Why is it important that different raw materials in a blast furnace flow in opposite directions?
4. What reactions occur in a blast furnace (a) between gases and solid materials, (b) between solids?

5. What are the advantages of fluxed sinter over formerly used mixtures?
6. On what do the temperature conditions of a blast furnace depend?
7. Name all methods by which the reaction occurring in a blast furnace can be accelerated.
8. How can the consumption of coke be decreased?
9. Why cannot finely divided materials be loaded directly into a blast furnace?
10. One blast furnace is usually served by three air heating plants. Explain why.
11. The usefull capacity of a blast furnace is 2700 m^3 and its utilization coefficient is 0.80. What is the daily output of the furnace?
12. Which of the principles underlying the blast furnace process can be regarded as general principles of chemical manufacture? Which of these can be regarded as principles common to all industrial processes?

7.9

Manufacture of Steel

Pig iron produced in a blast furnace and iron scrap are used as raw materials for the production of steel.

Pig iron intended for conversion into steel is called *conversion iron* and its composition varies within wide limits. Conversion iron contains maximum 4.4% of carbon, 1.75% silicon, 1.75% manganese, 0.30% phosphorus and 0.03% sulphur. The contents of carbon, silicon and manganese must be decreased down to tenths of one per cent for steels. Steel should contain as little sulphur and phosphorus as possible since these elements make the steel brittle: sulphur makes the steel brittle when it is hot, and phosphorus when it is cold.

The conversion of pig iron into steel is attained through oxidation at high temperatures. The source of oxygen is air and iron oxides contained in the metal scrap and iron ore that are added to pig iron.

Iron prevails in cast iron and it partly oxidizes

$$2Fe + O_2 = 2FeO + Q$$

Iron(II) oxide mixes with the molten metal and oxidizes silicon, manganese, phosphorus, and carbon:

$$Si + 2FeO = SiO_2 + 2Fe + Q,$$
$$Mn + FeO = MnO + Fe + Q,$$
$$2P + 5FeO = P_2O_5 + 5Fe + Q,$$
$$C + FeO = CO + Fe - Q$$

Phosphorus(V) oxide combines with calcium oxide and sulphur then converts calcium into calcium sulphide.

When oxidation reactions have completed, the liquid alloy still contains iron(II) oxide which has to be separated. Moreover, the concentration of

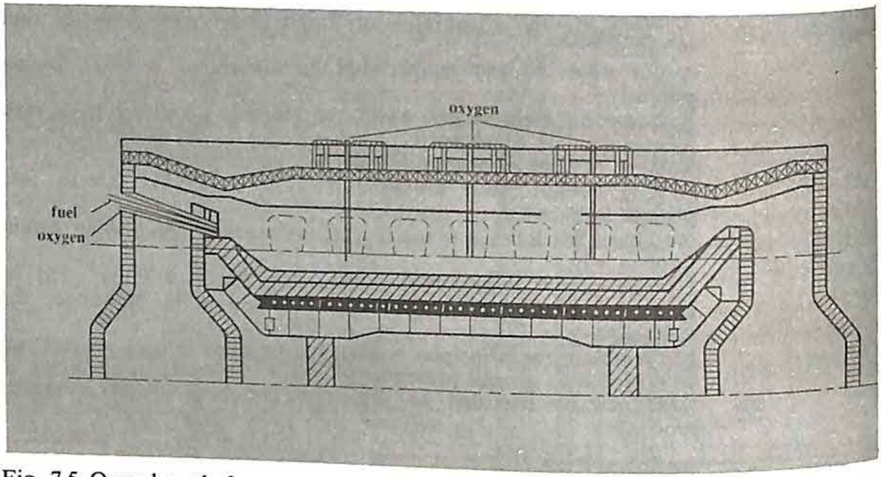

Fig. 7.5 Open-hearth furnace

carbon, silicon and manganese in the steel must be adjusted to the required level. This is attained by adding *deoxidizers*, e. g. ferromanganese (an alloy of iron and manganese), ferrosilicon, or aluminium. Manganese, for example, reacts with ferrous oxide

$$\mathrm{Mn + FeO = MnO + Fe}$$

What are the right conditions for obtaining high grade steel with the minimum loss of heat per unit weight of steel, the maximum reaction rate, and with the highest possible efficiency?

The conversion rate can be accelerated by adding oxygen to the air, or completely substituting oxygen for air, by increasing the concentration of the reactants, and by simultaneously elevating the temperature. Moreover, if oxygen is used, the quality of the steel improves significantly because the concentration of nitrogen dissolved in it decreases.

The rate of this process, in which gases, liquids, and solids are involved, depends greatly on the contact surface area between the reactants. This should be as great as possible.

The reaction should be carried out at as high a temperature as possible in order to accelerate the melting of the solid components and to increase the rate of all the other reactions.

Steel is produced industrially by three methods: the basic oxygen process (the process is carried out without use of any external heat source, the heat required coming from the exothermic reaction), the open-hearth process (the heat coming from burning fuel), and the electric furnace process.

The basic *oxygen process* is carried out in a converter (see page 181) lined on the inside with refractory bricks. This is a batch apparatus. Scrap and molten pig iron are loaded through the throat of the converter and oxygen under the pressure of 1 MPa is delivered through a tuyere. Oxygen may be blown from the bottom or through and across the molten metal. Lime is added by portions during the process.

The temperature increases due to the heat of the exothermic reactions. Owing to the large surface area across which oxygen and liquid iron contact each other, and also because of the high temperatures, silicon, manganese, carbon, and other elements are rapidly oxidized out.

The process continues for 30–40 minutes and then the barrel of the converter is tilted and the steel and slag are discharged separately.

Oxygen converters are highly efficient and yield high grade steel. Most of the steel in the Soviet Union is produced in converters.

The open-hearth process. The main source of heat in an open-hearth furnace is gaseous or liquid fuel (black oil). The process is therefore flexible and can be used to convert cast iron into various grades of steels. The furnace (Fig. 7.5) is a shallow hearth with a low roof of refractory bricks. The front wall of the furnace has openings through which the charge is mechanically loaded into the furnace. The opening through which the steel is discharged is located in the back wall. On both sides of the furnace there are channels through which the fuel and air are fed and the combustion products are discharged.

In order to increase the temperature of the flame, gaseous fuel and air are preheated in regenerators.

The consumption of fuel decreases and efficiency of the furnace increases when oxygen is used. It is added to the air or fed directly into the liquid bath.

The process takes about 12 times as long as that in an oxygen converter. The cost of construction of an open-hearth furnace is much greater than of the oxygen converter, and the production capacity of an open-hearth furnace is much lower. However, raw materials with any chemical composition can be processed in an open-hearth furnace and various kinds of fuels can be used in it, the grade of steel produced being only slightly lower than that of the steel obtained in converters.

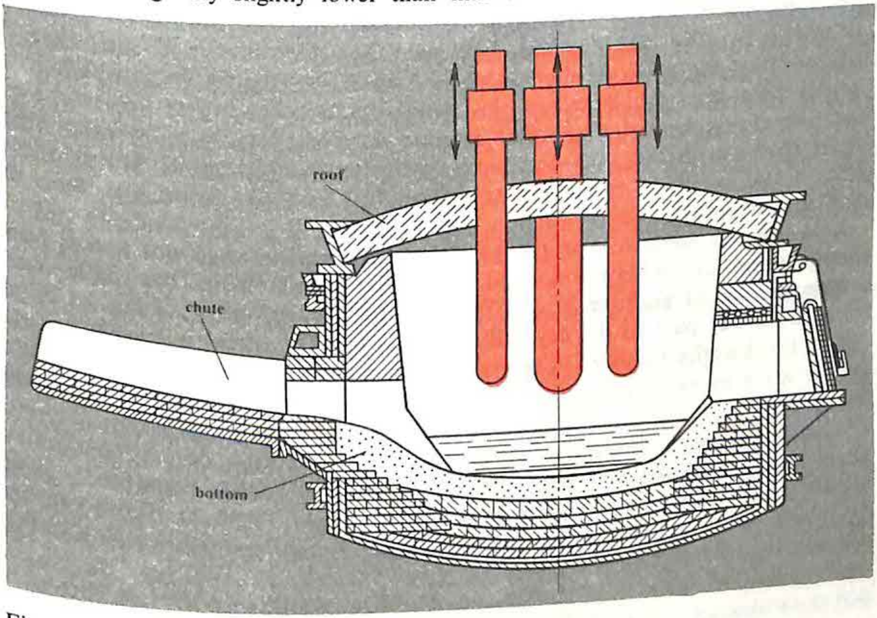

Fig. 7.6 Arc furnace

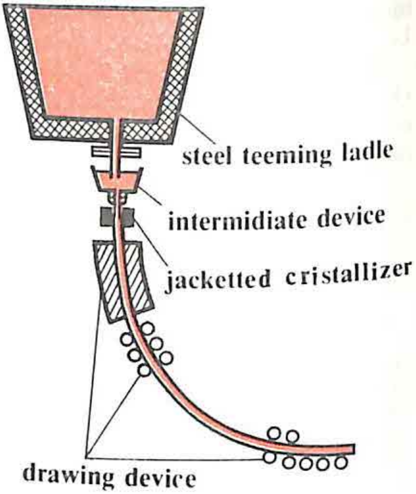

Fig. 7.7 Continuous teeming of steel

Obtaining steel in electric furnaces. Using electricity as the source of heat in the manufacture of steel ensures higher temperatures and easier control of the reducing and temperature conditions. Any steel can be smelted in electric furnaces but they are especially useful for making alloy steels as the losses of alloying elements in electric furnaces are lower than they are in other types of furnaces. Steels containing high-melting metals such as tungsten and molybdenum can be produced in these furnaces.

Electric arc furnaces (Fig. 7.6) are mainly used in industry. Heat is generated by the arc formed between the electrodes and the charge.

Teeming of the steel. Molten steel is poured into ladles from which it is then teemed into molds where the metal crystallizes. Ingots are extracted from the molds, heated, and rolled in blooming or slabbing mills. Processing liquid steel into billets includes many operations each of which is a periodic process and involves much labour. Much fuel and significant quantities of steel are also lost.

A *continuous method of preparing billets* has been worked out and is now widely used in industry. Liquid steel is teemed from the ladle into a water-cooled crystallizer (Fig. 7.7). A special drawing device pulls the billet from the lower part of the crystallizer and when the metal is cool it can be cut to the lengths required. The continuous pouring of steel is cheeper than the iterative process. The entire procedure is shorter and the quality of steel better.

The metallurgical processes we have just discussed are especially effective when they are united in a chain of operations, viz. charge preparation from fluxed sinter, use of oxygen and natural gas in blast furnaces, transportation of liquid cast iron to oxygen converters, and finally steel molding using continuous teeming devices.

Even so the conversion of iron ore into steel via these processes is overall not a continuous process. The ores are first converted into pig iron from which steels are finally obtained. This interferes with the production of high-grade steels because undesirable impurities may be added to steels at each step.

At the present time scientists and engineers are working hard to develop a method of directly and continuously converting iron ore into steel. One of the proposed methods is first to crush the ore to powder, mix it with a binding agent, and roll it into small balls (pellets). The pellets are dried, fired, and loaded into the top of vertical shaft furnace while hot gas consisting of carbon monoxide and hydrogen is fed in from the bottom. The ore is reduced in the pellets and the free iron is converted easily into alloy steel:

?

1. What does the reaction rate during conversion of pig iron into steel depend on, and how can the reaction rate be changed?
2. What effect does oxygen have on the steel smelting process?

7.10

Manufacture of Aluminium

Aluminium was discovered and obtained in the free state in 1825 via the reaction between potassium and aluminium chloride, i.e. by the metallothermic process. Industrial manufacture of aluminium started in 1854 and sodium was then used as the reducing agent. This process, however, was expensive (why?).

The manufacture of aluminium began to increase rapidly after discovery of the electrolysis method, the first plant being started in Switzerland in 1888. Aluminium is obtained from aluminium oxide, which melts at a very high temperature (2050°C). A solution of aluminium oxide in molten cryolite Na_3AlF_6 melts at relatively low temperatures and has high electrical conductivity. This solution is therefore used for electrolysis. At temperatures about 950°C small amounts of aluminium dissolve in the electrolyte, but the solubility of aluminium increases rapidly with temperature, and significant loss of aluminium becomes inevitable.

Liquid aluminium is liberated at the cathode during electrolysis

$$Al^{3+} + 3\bar{e} = Al^0$$

and carbon oxides are formed at carbon anodes that are used in industrial electrolyzers.

Iron and silicon react with aluminium to form compounds that decrease its ductility and stability to corrosion. Hence only pure aluminium oxide free from iron oxides or silicon(IV) oxide should be used for electrolysis.

Bauxite is the main ore of aluminium and extensive deposits of this mineral are worked in the Soviet Union in the Urals, near Leningrad, and in Northern Kazakhstan. Aluminium is also produced in this country from nepheline, the alkaline aluminosilicate whose deposits are found in the Kola Peninsula, and in the Kemerovo and Krasnoyarsk regions. The ores quarried in the Kola Peninsula contain also apatite, which is a valuable raw material for the manufacture of phosphorus fertilizers. Hence the wastes from the apatite ores are used for the recovery of the nepheline concentrate, which is then turned into aluminium oxide. The alkalis contained in the ores are used to make potash and soda, and the silica is used for the manufacture of cement.

An industrial electrolyzer shown in Fig. 7.8 is a rectangular steel bath lined on the inside with refractory bricks and carbon blocks. Steel rods extend from outside the bath down to the lower blocks. Molten aluminium collects on the bottom of the bath and acts as the cathode. On top of the molten aluminium lies a layer of molten electrolyte into which the carbon anode is lowered. Electric current is applied to the anode through steel rods. The anode burns up gradually and must therefore be extended: carbonaceous mass is loaded into the aluminium case of the anode. Some electrolyte solidifies because it is cooled by the surrounding air (from top and sides). The crust that forms is broken up to make holes through which gases formed during the electrolysis can escape.

The electrolyzer operates continuously but the aluminium oxide is loaded into the bath in batches, which are placed on top of the crust formed by the solidified electrolyte. The crust is broken up by pneumatic hammers. The accumulated aluminium is discharged every 2 or 3 days. Molten aluminium is poured into a ladle (Fig. 7.9) which has been evacuated preliminarily. Molten aluminium is sucked up into the ladle through a pipe and then distributed from the ladle into molds.

A great deal of electricity is required for the manufacture of aluminium, the best electrolyzers consuming 15 000 kw · hr per ton of aluminium. If the capacity of an electrolyzer is increased, the loss of heat into the environment decreases and the specific consumption of energy decreases; mechanization of

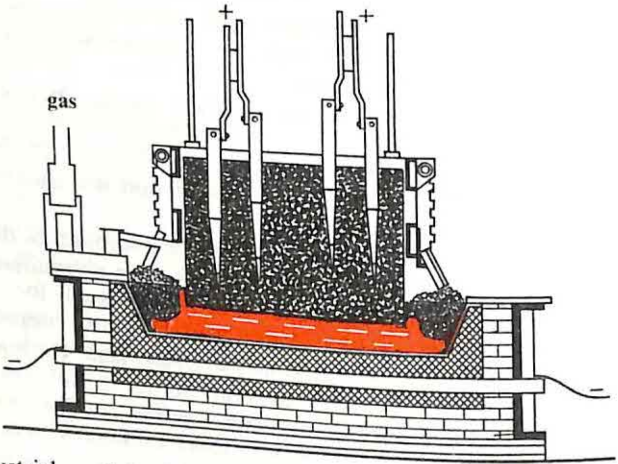

Fig. 7.8 Industrial electrolyzer for smelting of aluminium

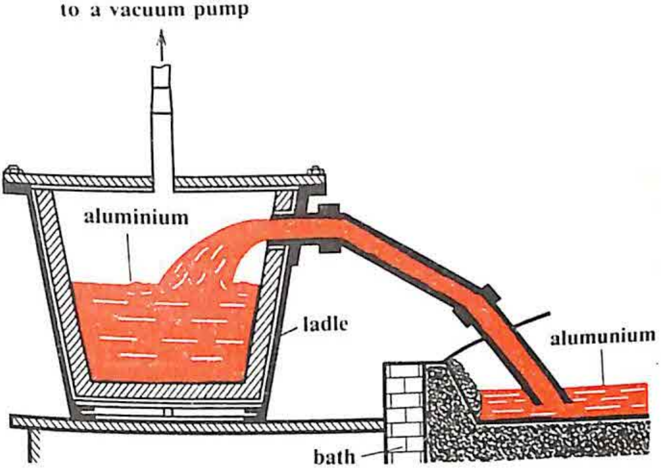

Fig. 7.9 Vacuum ladle for extraction of aluminium from the bath

separate steps of the process becomes easier, and the efficiency of the labour increases.

Controlling an electrolysis is difficult because the composition of the electrolyte is always changing during the process, the raw materials are loaded and aluminium is discharged periodically, etc.

The development of the aluminium industry in the Soviet Union is associated with the realization of the electrification plan worked out by V. I. Lenin. The first Soviet aluminium plant was built in 1932 at Volkhov and was named after S. M. Kirov.

Aluminium obtained by electrolysis contains iron, silica, and other nonmetal and gaseous impurities. Purer aluminium is obtained by repeated melting and electrolysis. Duralumins, the alloys of aluminium with copper, manganese, and magnesium, are widely used to make sheets, wires, and tubes. Silumins, alloys of aluminium with silicon, are used as foundry alloys because they are readily welded.

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1. What are the requirements for the electrolyte used in the manufacture of aluminium?
2. In order to obtain 1 ton of aluminium, 1.92 tons of aluminium oxide was used up. What is the loss of aluminium oxide?

7.11 Development of Metallurgy in the Soviet Union

In 1913 Russia was the fifth largest producer of cast iron and steel in the world. Much has been done to increase the production of these metals after the Great October Revolution, and the

Soviet Union is now the largest producer of pig iron and steel, and nonferrous metals are produced in great quantities too. The growth in the production of metals in the Soviet Union is unrivalled. The development of the metallurgical industry in this country is backed by the richest deposits of raw materials. Further development of metal production in the Soviet Union depends on advances in science and technology. The Programme of the Communist Party of the Soviet Union provides for the further development of the metallurgical industry in this country. Old plants will be modernized and new large plants established in Siberia, Kursk region, and in Kazakhstan.

■ Using material of this chapter, and also knowledge you have gained from other subjects, prepare a report on the role of the metallurgical industry in the development of the economy and the well-being of people. Indicate ways for further progress in metallurgy and the effects that metallurgy has on the economy.

8 General Scientific Principles of Chemical Manufacture

We have studied inorganic chemistry and got acquainted with some of the most important fields of its application in industry and agriculture, and we know about the role of chemistry in the development of economy. We have also become acquainted with some general principles underlying the chemical manufacture and the manufacture of goods in general. Let us try to draw some conclusions.

8.1 Connections Between Science and Technology

We already know from chemistry, physics, biology, and other subjects, that the manufacture of various goods in the Soviet Union is increasing. This is supported by data concerning the development of chemical manufacture and metallurgy in recent years.

1. Characterize the most important advances in the manufacture of sulphuric acid from the point of view of (a) raw materials, (b) intensification of pyrite roasting and (c) oxidation of sulphur(IV) oxide.
2. What improvements in the blast furnace and steel smelting processes have substantially changed the requirements for coke, increased the production capacity of blast furnaces, accelerated significantly the process of steel manufacture, and increased the efficiency of steel smelting furnaces?
3. What has stimulated other advances in metallurgy? Why were these advances intensively incorporated into industrial practice?

All these occurrences can be explained by the substantial change in the relationship between science and technology. Not long ago, many technological improvements were the result of long empirical search. Now science has achieved a stage at which material production can be improved on the basis of scientific advances. Theoretical advances, the discovery of new phenomena and new regularities underlie modern progress in science and technology. Theoretical chemistry and mathematics are the foundations upon which developments in the chemical manufacture are based.

The effect of the theory of chemical equilibrium and chemical kinetics is a vivid example of the importance of theory for practical chemical manufacture.

However, in order to convert theoretical advances into developments in industry, it is not only necessary to know the structure of matter, but also the laws of chemical reactions. It is necessary to know how can this or that reaction be realized in a more rational way in industrial conditions, how to obtain products with the desired properties at the lowest possible cost and with the highest possible labour productivity. The following questions should be answered: from what materials and by what reactions can a given product be reasonably obtained? What are the requisite conditions for the maximum possible reaction rate and the maximum possible yield of the product? Which flowsheet, what equipment and which apparatus must be used to obtain the highest possible effect? How can the process be effectively controlled? What measures should be taken to ensure the appropriate good working practices of the process and safe handling of noxious and hazardous substances?

All these problems are the subject matter of *chemical engineering* which in turn includes some independent sciences. Owing to the development of technology, the discovery of new laws and phenomena, it has become possible to realize quickly the advances in the sciences. The synthesis of ammonia has become possible after the discovery of a rational method by which the reaction is realized at unfavourable equilibrium (circulating method). Gigantic towers, having the capacity of 1 500 tons of ammonia a day, are now constructed.

The connection of science and technology in our days can be characterized by the following formula: science turns into a productive force.

8.2

Some Principles of Chemical Technology

When we discussed the manufacture of important chemical products such as sulphuric acid, ammonia, nitric acid, mineral fertilizers, pig iron, steel, and aluminium, we got to know some general principles of chemical technology. Now we can draw certain conclusions and formulate them.

The selection of the proper *raw material* is very important. Chemical and metallurgical industries can turn out the same product from different raw materials. Various processes are used in industry to prepare raw materials and to process them: raw materials are concentrated, purified, etc. *Complex utilization of raw materials* is very important in solving the problem of raw materials.

1. Name raw materials used in metallurgical and chemical industries.
2. What are the criteria for the selection of raw materials for chemical processes we have studied?
3. Explain the importance of complex utilization of raw materials.
4. Give examples of preparing raw materials in the chemical industry: concentration, size reduction, size enlargement by sintering, etc.

The theory of chemical equilibrium determines the dependence of the *equilibrium*, i.e. maximum possible *yield of a product* on the concentration of the reactants, the temperature of the process, and the pressure. A theory saves a fruitless search in 'prohibited' fields of chemical equilibrium, and secondly, it defines the conditions under which the wanted product can be obtained. We have seen one such futile search people made when they were looking for a way to synthesize ammonia.

1. Describe the main reasons for the failure of the century-long laboratory research for the synthesis of ammonia, which is now solved by a simple process.
2. In this connection, formulate the principle underlying the manufacture of products at high yields in conditions when it is impossible to shift the equilibrium in the desired direction.

It is very important to know if a given reaction is reversible or irreversible and how the equilibrium yield depends on the conditions. It is also necessary to have data on the *rate of the process*. Chemical kinetics gives us most of the data required for selection of conditions under which a given reaction should be effectively carried out and for correct design of the apparatus.

1. Consider the criteria for the selection of the optimum concentration of the reactants during (a) pyrite roasting, (b) absorption of sulphur(VI) oxide, (c) synthesis of ammonia.
2. Compare the processes in which the contact area between reactants is made as large as possible. Which methods are used to increase the surface area of the reactants?
3. What are the criteria for determining the optimum temperature for (a) pyrite roasting, (b) oxidation of sulphur(IV) oxide, (c) synthesis of ammonia, (d) formation of nitric acid from nitrogen oxides, (e) steel smelting?
4. What are the criteria for determining the optimum pressure for (a) synthesis of ammonia, (b) preparation of nitric acid?
5. What are the principles of catalytic reactions? Consider three reactions: the oxidation of sulphur(IV) oxide, the synthesis of ammonia, and the oxidation of ammonia.

We have only covered a few industrial processes but it has become already clear that *flowsheets* and apparatus used in chemical manufacture are quite varied. This is due to the variety of properties of raw materials and conditions under which they are turned into chemical products. We shall only discuss three topics now.

1. A comparison of continuous and batch processes and the advantages and disadvantages of both.
2. Why is it reasonable to use high capacity apparatus in metallurgy and chemical manufacture?
3. What are the advantages of the countercurrent process flows?

In order to increase labour efficiency and to reduce the cost of a product, chemical manufacture is *mechanized*.

Modern chemical manufacture cannot do without control instruments which give information about the process temperature and pressure, the weights and volumes of the process materials, the levels of liquids in apparatuses, the flow rates of materials through the apparatus, the composition of the starting substances, the quality of the products obtained, etc. To make the inspection and control easier, all this information is delivered to the central control board. Recording instruments are installed on the control board alongside the controls which are used to adjust the process conditions. These controls are, for example, valves governing flows of liquids and gases into the apparatus, instruments controlling heating, etc. The *centralized location of the controls* makes the overall management of the process equipment easier.

A more perfect control system is that in which the process conditions are maintained *automatically*. Automatic controls maintain present temperature, pressure, concentration, etc. The duty of the operator is only to start the process and to remedy faults if any. Automation of the process increases labour efficiency while the process conditions become stabilized. This is very important for high yields and the quality of the products. Many modern plants producing sulphuric acid and nitrogen products are fully automated in the Soviet Union.

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1. What are the criteria for selection of raw materials for a given chemical manufacture in a given region?
2. What is the importance of (a) a chemical equation, and (b) a thermochemical equation for a chemical manufacture.
3. Which conditions are optimum for a given chemical process?
4. Give the criteria for selecting the optimum temperature for (a) pyrite roasting, (b) oxidation of sulphur(IV) oxide, (c) absorption of sulphur(VI) oxide.
5. In what way can a catalyst be considered optimal?
6. Explain the advantage of using large-capacity chemical apparatus.
7. What is the difference between batch and continuous processes? Give examples of process units of both types, using the experience of your laboratory exercises.
8. Give examples of processes where the countercurrent flow of processed materials is used. Explain the advantages of this principle.
9. What is the purpose of the packing in absorbing towers? What is an absorbing tower?
10. How can the heat of chemical reactions be utilized? Give examples.

I. Laboratory Exercises

1. Exchange reactions between electrolyte solutions

Exercise 1. Place 2-3 ml of ferric chloride solution into a test tube and add an equal volume of aqueous sodium hydroxide. Observe the reaction. Write the complete and net ionic equations for the reaction.

Exercise 2. Place 1-2 ml of sodium sulphite solution in a test tube and add an equal volume of sulphuric acid. Heat slightly. Carefully smell the gas that evolves. Name the gas. Hold a moist strip of blue litmus paper over the mouth of the test tube and observe the colour change. Explain. Write the complete and net ionic equations for the reactions.

Exercise 3. Place 2-3 ml of sodium hydroxide solution into a test tube and add 2-3 drops of phenolphthalein. Observe the colour change and explain it. Add sulphuric acid in small portions, stirring the solution all the time until the colour vanishes. Explain discolouration of the solution. Write the complete and net ionic equations for the reactions.

Exercise 4. Obtain the necessary reagents from your teacher and prepare (a) cupric hydroxide, and (b) barium sulphate. Write the complete and net ionic equations for the reactions.

2. Testing salt solutions by indicators

Place some aluminium chloride solution into one test tube, sodium carbonate solution into another, and sodium chloride solution into the third test tube. (The volume of each solution is 1 ml.) Rinse a glass rod with distilled water and transfer a drop of each solution onto pieces of blue and red litmus paper. Explain the colour changes, if any. Write the complete and net ionic equations for the reactions.

3. Reaction of ammonium salt with alkali

Place 2-3 ml of ammonium sulphate solution into a test tube and add an equal volume of sodium hydroxide solution. Heat the mixture to boiling and carefully smell the evolving gas. Hold a moist piece of red litmus paper over the mouth of the test tube. Explain the change in the colour of the paper. Write the reaction's equation.

4. Acquaintance with properties of orthophosphoric acid, phosphates, and hydrogen phosphates

Exercise 1. Place 10-15 ml of lime water in a beaker and add, drop by drop, orthophosphoric acid solution (diluted 1 : 20) stirring the mixture continuously: the solution becomes cloudy due to the formation of insoluble calcium phosphate. The cloudiness soon disappears because water-soluble calcium dihydrogen phosphate is formed:

$$Ca_3(PO_4)_2 + 12H^+ + 4PO_4^{3-} = 3Ca^{2+} + 6H_2PO_4^-$$

Exercise 2. Place calcium phosphate in one test tube, calcium hydrogen phosphate in another, and calcium dihydrogen phosphate into the third test tube. Place 1/4 teaspoonful of each salt. Add 5 ml of water to each salt and observe the reactions. Explain.

5. Acquaintance with nitrogen and phosphorus fertilizers. Identification tests for ammonium salts and nitrates

Exercise 1. Examine the samples of mineral fertilizers obtained from the teacher. Pay special attention to their different colours and the crystalline structures of most of them.

Place 1/4 teaspoonful of each fertilizer into different test tubes, add 5 ml of distilled water into each test tube and stir. Are the fertilizers equally soluble? Write the results of your observations in a table like this one:

Fertilizer	Chemical formula	Appearance	Solubility in water at normal temperature

Exercise 2. Carry out reactions to prove the composition of ammonium nitrate. Place 1/4 teaspoonful of ammonium nitrate in a test tube and add the same amount of copper shavings. Add (carefully!) a few drops of concentrated sulphuric acid and observe the reaction. Which ions in the ammonium nitrate indicate that the reaction occurs? Write the reaction equations.

Place 2-3 ml of ammonium nitrate solution into another test tube and test it as described in subsection 3, page 163.

6. Acquaintance with properties of carbonates and bicarbonates. Test for carbonate ion

Exercise 1. Place small amounts of sodium carbonate, magnesium carbonate, and sodium bicarbonate into three separate test tubes (the salts should only cover the bottom of the test tube). Add 1 ml of dilute hydrochloric acid to each salt and observe the reaction. Put a burning match into each test tube and observe. Write the ionic equations for the reactions between carbonates and hydrochloric acid (both complete and net equations).

Exercise 2. Assemble the apparatus as shown in Fig. I.1. Place sodium bicarbonate in a test tube to fill up about one tenth of its volume. Plug the tube with a stopper that has a glass tube through it, and fix in the clamp of a stand so that the test tube's stopper end is slightly below the other end. (Why do we fix the apparatus in this position?) Lower the end of the outlet tube into the bottom of another test tube that is about 1/4 full of lime water. First gently heat the entire test tube and then strongly heat the sodium bicarbonate. Observe the changes in the salt and in the lime water. As soon as the lime water becomes cloudy, lift the apparatus up and put it aside; turn off the burner. Which substances have formed during calcining of sodium bicarbonate? Which reaction occurred when carbon dioxide was passed through the lime water? Write down the reaction equations.

Exercise 3. Place 1 ml of sodium carbonate solution into a test tube and add an equal volume of barium chloride solution. Observe the reaction. Write the ionic equations for the reactions (both complete and net equations).

Add about 1 ml of dilute hydrochloric acid to the precipitate and observe the reaction. Write down the complete and net ionic equations for the reactions.

Exercise 4. Place 1 ml of sodium carbonate solution into a test tube and add a few drops of silver nitrate solution. Observe the reaction. Write down the complete and net ionic equations.

Add 0.5 ml of dilute nitric acid to the precipitate and observe. Which gas is evolved? Write down the complete and net ionic equations for the reactions.

Exercise 5. Obtain from the teacher three test tubes containing solutions of a chloride, a carbonate, and a sulphate. Identify experimentally the carbonate. Write the net ionic equation for your reaction. Which reagent can be used to test for the carbonate ion?

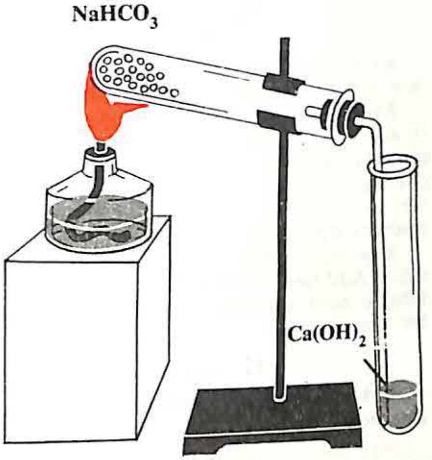


Fig. I.1 Apparatus for decomposition of sodium bicarbonate

7. Testing carbonate and silicate solutions using indicators

Exercise 1. Place 1 ml of sodium carbonate and the same amount of sodium silicate into two different test tubes. Rinse a glass rod with distilled water and transfer a drop of each solution onto pieces of red litmus paper. Observe the colour changes. What conclusion concerning the strength of carbonic and silicic acids can be derived from this experiment? Write down the equations for the hydrolysis of the salts.

8. Reaction of metals with salt solutions

Exercise 1. Place about 2 ml of zinc chloride solution into one test tube and 2 ml of copper(II) chloride solution into another. Drop a grain of copper into the first test tube and a grain of zinc into the second test tube: observe the reaction. In which test tube do you notice any changes that might indicate a reaction?

Exercise 2. Place a solution of copper sulphate into one test tube and ferric sulphate solution into another. Add some iron shavings into the first and a grain of copper into the second. Make the same observations as in the previous experiment.

Note the salts with which zinc and iron react. Will a solution of ferric sulphate react with zinc?

9. Alloys

Examine the specimens of alloys obtained from the teacher. Pay attention to the lustre, colour of the surface of alloys, and to their hardness, which is greater than that of the metals from which they are formed.

10. Colouring flames by sodium and potassium salts. Acquaintance with important salts of sodium and potassium

Exercise 1. Place 10 ml of sodium chloride solution into a test tube and the same volume of potassium chloride solution into another test tube.

Hold an iron wire in the flame of a burner until it is red hot. Dip the wire into the sodium chloride solution and put it back into the flame. What is the colour of the flame?

Rinse the wire in hydrochloric acid and calcine it again. Dip it in the potassium chloride solution and put it back into the flame. What is the colour of the flame now?

Exercise 2. Examine specimens of pure salts of sodium and potassium and also minerals containing these salts. Compare their colours, crystal structures, and make your conclusions.

11. Natural calcium compounds. Conversion of calcium carbonate into calcium bicarbonate and vice versa

Exercise 1. Examine specimens of natural calcium compounds. Pay attention to their colour, crystal or amorphous structure, transparency, hardness, etc.

Exercise 2. Assemble the apparatus for preparing carbon dioxide. Place about 10 ml of lime water into a test tube and pass carbon dioxide through it until the solution becomes cloudy. What substance has formed in the solution? Continue passing carbon dioxide through the solution until it turns clear. What reactions occur when carbon dioxide is passed through lime water for a long time? Write down reaction equations.

Exercise 3. Place some calcium bicarbonate solution into three separate test tubes. Add lime water to one, sodium carbonate to the other, and heat the third test tube to boiling. Observe the reaction and explain. Write out the net ionic equations for the reactions.

12. Acquaintance with aluminium and its alloys

Examine specimens of aluminium and its alloys, paying attention to appearance of the metals and their ductility.

13. Obtaining aluminium hydroxide and studying its properties

Exercise 1. Place 2-3 ml of an aluminium salt solution into two test tubes and add equal volumes of an aqueous solution of ammonia. Observe the reaction. Write down the net ionic equations.

Exercise 2. Gradually add hydrochloric acid to one test tube containing precipitated aluminium hydroxide and shake. Observe the reaction and explain it. Write the net ionic equation for the reaction.

Exercise 3. Add sodium hydroxide solution, by small portions, to the precipitate of aluminium hydroxide in the other test tube and shake. Observe the reaction and explain it. Write the net ionic equation of the reaction.

14. Pig iron and steel

Examine specimens of pig iron and steel, paying special attention to the colour of their surfaces, the presence or absence of lustre, and to their magnetic properties.

15. Reaction of iron hydroxides with acids

Exercise 1. Obtain the necessary reagents from your teacher and prepare ferrous and ferric hydroxides. Write the net ionic equations for the reactions.

Exercise 2. Try the action of acids on the prepared iron hydroxides. Write the net ionic equations for the reactions.

16. Qualitative tests for doubly and triply charged iron ions

Exercise 1. Add potassium thiocyanate (KCNS) solution, a salt of thiocyanic acid (HCNS), to a solution of ferric hydroxide. Observe the colour change. Write the net ionic equation of the reaction remembering that one reaction product, viz., ferric thiocyanate $Fe(CNS)_3$, only sparingly dissociates into ions.

Exercise 2. Add a solution of potassium ferricyanide $K_3Fe(CN)_6$ to a solution of ferrous chloride. Observe the reaction and write the net ionic equation remembering that one of the reaction products, viz., Turnbull's blue $Fe_3[Fe(CN)_6]_2$, precipitates.

II. Practical Experiments

Experiment 1 Solving Problems About the Dissociation of Electrolytes

Problem 1. Carry out the reactions between solutions of (1) Na_2CO_3 and HNO_3, $CuCl_2$ and KOH, NaOH and H_2SO_4; (2) Na_2SO_3 and HCl, $MgCl_2$ and NaOH, KOH and HNO_3; (3) Ka_2CO_3 and H_2SO_4, $CuSO_4$ and KOH, NaOH and HCl. Write the ionic equations for the reactions and explain them.

Problem 2. Place 1 ml of the following solutions into test tubes: (1) $Pb(NO_3)_2$, Na_2CO_3, KCl; (2) $ZnSO_4$, Na_2S, $NaNO_3$; (3) $AlCl_3$, K_2CO_3, Na_2SO_4. Test each solution with litmus paper. Explain the results of your tests and write the ionic equations for the reactions.

Problem 3. Carry out reactions between (a) hydrochloric acid and zinc, (b) potassium iodide solution and chlorine water, (c) sodium sulphide solution and bromine water. Write the ionic equations for the reactions (both complete and net equations) and indicate which reagents were oxidized and which reduced in each reaction.

Problem 4. Prepare the following: (a) barium sulphate, (b) ferric hydroxide, and (c) magnesium carbonate. Write the complete and net ionic equations for the reactions and explain them.

Experiment 2 Preparing Ammonia and Experiments with It. Properties of Aqueous Solution of Ammonia

1. Assemble the apparatus as shown in Fig. II.1. Place some ammonium chloride and calcium hydroxide (one teaspoonful of each) onto a sheet of paper or into a small porcelain dish (a crucible). Mix the salts with a glass rod and transfer them into a dry test tube. Close it with a stopper through which a glass tube is passed and fix in the stand. The test tube should be inclined to its stoppered end. Adjust another dry test tube over the gas outlet tube to collect ammonia.

First heat the entire test tube with a burner (2-3 passages in the flame) and then strongly heat the part of the test tube containing the mixture of ammonium chloride and calcium hydroxide. To detect the presence of ammonia, bring a piece of moist phenolphthalein paper close to the mouth of the overturned test tube. When the overturned test tube is full of ammonia, dip a glass rod into concentrated hydrochloric acid and hold it over the mouth of the test tube. Observe the reaction and write out its equation.

Discontinue heating the mixture. Carefully remove the test tube containing ammonia from the gas outlet and stopper the outlet immediately with a piece of wet cotton wool.

Table II.1

Identification of Mineral Fertilizers

Fertilizer	Appearance	Solubility in water	Reactions with				Flame test
			sulphuric acid and copper	barium chloride solution and acetic acid	alkali (when heated)	silver nitrate solution	
1. Ammonium nitrate	White crystals, sometimes a yellowish mass or granules	Good	Brown gas evolves	–	Smell of ammonia	–	Yellow (due to impurities)
2. Sodium nitrate	Large colourless crystals	Good	Brown gas evolves	Slight turbidity (due to impurities)	No smell of ammonia	Meagre precipitate (due to impurities)	Yellow
3. Ammonium sulphate	Small light-gray crystals	Good	Brown gas does not evolve	White substance insoluble in acetic acid precipitates	Ammonia evolves	Slight turbidity	–
4. Super-phosphate	Light-gray powder or granules	Partial	Brown gas does not evolve	White substance, partly soluble in acetic acid, precipitates	No smell of ammonia	Yellow substance precipitates	Yellow (due to impurities)
5. Sylvinite	Pink crystals	Good	Brown gas does not evolve	–	No smell of ammonia	White substance precipitates	Yellow. When flame is viewed through a blue filter, flame is violet
6. Potassium salt	Colourless crystals	Good	Brown gas does not evolve	–	No smell of ammonia	White substance precipitates	Yellow. When viewed through a blue filter, flame is violet

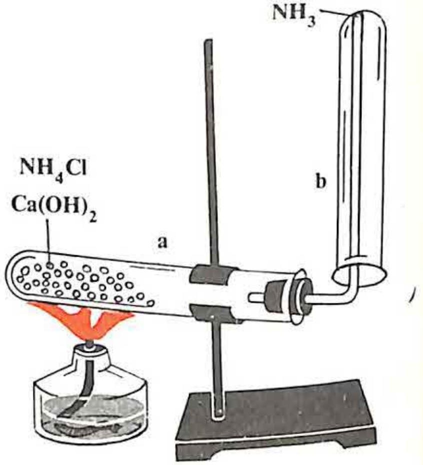


Fig. II.1 Apparatus for preparing ammonia

Close the test tube containing ammonia with your thumb, transfer the test tube into a dish filled with water, and release the thumb. Observe the reaction. Why does the liquid level rise in the test tube? Close the mouth of the test tube with your thumb again and remove it from the dish.

Answer the following questions: (1) Why should the test tube containing the reactants be fixed in an inclined position? Write down the equation of the reaction between ammonium chloride and calcium hydroxide for it will help you answer this question. (2) Why should ammonia be collected in an overturned test tube? What other gases can be collected in a similar way? (3) Suppose we dip a glass rod into concentrated nitric acid (instead of hydrochloric acid as in our experiment) and bring it to the mouth of the test tube. What would happen then? Write down the equation for this reaction. (4) How can the presence of ammonium ions in the aqueous solution of ammonia be proved?

2. Place 4-5 ml of ammonia solution into a test tube and add 2-3 drops of phenolphthalein solution. Observe the colour change. Heat the solution to boiling and observe the change in the colour again. Explain the colour changes. Write down equations for the reactions.

3. Place 4-5 ml of ammonia solution into a test tube and add 2-3 drops of phenolphthalein solution. Now add sulphuric acid drop by drop until the crimson colour vanishes. Explain the discolouration of the solution. Write the ionic equations for the reaction (both the complete and net equations).

4. Place 2-3 ml of aluminium chloride solution into a test tube and add the same volume of ammonia solution. Observe the changes. Write ionic equations.

Experiment 3 Identifying Mineral Fertilizers

1. Draw Table II.1 given on page 169 and fill in the names of fertilizers.
2. Obtain a set of numbered fertilizer specimens.
3. Carry out experiments on each specimen as described in Table II.1 and fill in the results.
4. Compare your results with the tabulated data to identify the fertilizers.

Experiment 4 Solving Problems on 'Nitrogen Subgroup'

Problem 1. Carry out reactions characteristic of (1) ammonia, (2) nitric acid, (3) ammonium nitrate.

Problem 2. Prove experimentally that ammonium nitrate and ammonium sulphate cannot be mixed with lime before adding them to soil. Explain why? Write down the reaction equations.

Problem 3. Prove experimentally that (a) ammonium chloride contains the NH_4^+ and Cl^- ions, (b) ammonium sulphate contains the NH_4^+ and SO_4^{2-} ions.

Problem 4. The following fertilizers are given: potassium chloride, ammonium nitrate, and superphosphate. Identify each substance by characteristic reactions.

Problem 5. Obtain some ammonia from a mixture of ammonium chloride, ammonium sulphate, and ammonium nitrate.

Problem 6. Carry out the reactions that are expressed by the following ionic equations: (1) $H^+ + OH^- = H_2O$; (2) $Ba^{2+} + SO_4^{2-} = BaSO_4\downarrow$; (3) $Ag^+ + Cl^- = AgCl\downarrow$.

Problem 7. Obtain copper nitrate via three reactions.

Experiment 5 Preparing Carbon Dioxide and Studying Its Properties. Identification of Carbonates

1. Place a few pieces of marble or chalk in a test tube or a small flask and add enough dilute hydrochloric acid to cover the marble. Close the test tube with a stopper through which a gas tube is passed. Pass the evolving gas through (a) water stained with litmus, (b) lime water, (c) calcium chloride solution. Observe the reactions. Write down the reaction equations.
2. Place 1 ml of sodium carbonate solution into a test tube and add an equal volume of barium chloride solution. Observe the reaction and write the reaction equations (both the complete and net equations).
3. Place 1 ml of sodium carbonate solution in a test tube and add a few drops of silver nitrate. Observe the reaction. Write out the complete and net ionic equations. Add 0.5 ml of dilute nitric acid to the precipitate. Observe the reaction. Write out the complete and net ionic equations for the reaction.

Experiment 6 Solving Problems on 'Alkali Metals and Calcium'

1. Three test tubes are given. One contains sodium carbonate, the other calcium chloride, and the third calcium hydroxide solution. Identify the substances experimentally.
2. Three test tubes contain crystals of sodium chloride, potassium chloride and calcium chloride. Identify the salts experimentally.
3. Carry out reactions to realize the following conversions:

$$CaCl_2 \rightarrow CaCO_3 \rightarrow Ca(HCO_3)_2 \rightarrow CaCO_3 \rightarrow Ca(NO_3)_2$$

Write the complete and net ionic equations for the reactions.

4. Carry out reactions to realize the following conversions:

$$NaOH \rightarrow Na_2SO_4 \rightarrow NaCl \rightarrow NaNO_3$$

Write the complete and net ionic equations for the reactions.

5. Solutions of potassium carbonate, calcium hydroxide, and sulphuric acid are given. Obtain precipitates of calcium carbonate and calcium sulphate. Write the complete and net ionic equations for the reactions.
6. A test tube contains lime water. Carry out reactions to realize the following conversions:

$$Ca(OH)_2 \rightarrow CaCO_3 \rightarrow Ca(HCO_3)_2 \rightarrow CaCO_3 \rightarrow CaCl_2$$

Write out the complete and net ionic equations for the reactions.

Experiment 7 Aluminium and Its Compounds

1. Place some grains or shavings of aluminium into two test tube and add 3-4 ml of hydrochloric acid to one and 3-4 ml of sulphuric acid to the other test tube. If no reaction occurs, heat the test tube slightly (carefully!) over a burner. Observe the reaction. Which gas is evolved? Write down the net ionic equations for the reactions and indicate which substances are oxidized and which are reduced in these reactions.
2. Place 2-3 grains of aluminium into a test tube and add a solution of sodium (or potassium) hydroxide. If no reaction occurs, heat slightly the test tube. Which gas is liberated? Write down the reaction equation.
3. Test a solution of aluminium sulphate (or aluminium chloride) using litmus. Draw your conclusion about the strength of aluminium hydroxide as a base. Write down the equation for the hydrolysis of the aluminium salt.

Experiment 8 Iron and Its Compounds

1. Try the action of hydrochloric, sulphuric, or nitric acids on ferric oxide. Observe the reactions and write out their net ionic equations.

2. Prepare a small quantity of ferrous hydroxide precipitate. Note the colour and observe its change when exposed to air. Explain the reaction and write its net ionic equation.

3. Pour about 2 ml of ferrous chloride solution into a test tube and add the same amount of chlorine water. Observe the colour change. Explain the reaction and write the net ionic equation. Which substance is oxidized and which is reduced in this reaction?

4. Test a solution of ferrous chloride or ferrous sulphate using litmus. Draw your conclusion on the strength of ferrous hydroxide as a base. Write the equation for the hydrolysis of ferrous sulphate.

Experiment 9 Solving Problems on 'Metals'

Problem 1. Chlorides of sodium, potassium and magnesium are given in three separate test tubes. Identify the salts experimentally.

Problem 2. Chlorides of iron(II), calcium, and barium are given in three separate test tubes. Identify the salts.

Problem 3. Solutions of aluminium chloride, ferric chloride, barium chloride, and ferrous sulphate are given in four separate test tubes. Identify the salts experimentally.

Problem 4. Prove experimentally that a sample of green vitriol contains ferric sulphate.

Problem 5. Prove experimentally that a given substance is ferric chloride.

Problem 6. Give reactions characteristic of ferrous and ferric ions.

Problem 7. Prepare aluminium hydroxide and prove its amphoteric properties experimentally.

Problem 8. A given sample of water contains substances which account for its carbonate and temporary hardness. Carry out experiments to soften the water.

Problem 9. Prepare ferric oxide from ferric chloride.

Problem 10. Prepare sodium aluminate solution from aluminium.

Problem 11. Prepape ferrous chloride from iron.

Problem 12. Chemically clean a rusted iron nail.

Answers to Problems Marked with an Asterisk

page	problem	answer
18	5	Read the definition of acids and bases.
18	6	Sodium ions prevail, while the hydrogen and hydroxide ions are contained in smaller amounts.
21	7	It is an electrolyte with coloured cations and anions.
24	5	Sodium sulphate and potassium nitrate.
43	5	Into the ammonium ion.
45	4	Ammonium hydrogen sulphate.
52	6	Ammonium nitrate.
62	7	Excess alkali is first present and a neutral phosphate is therefore obtained, which then turns into an acid phosphate.
62	9	A mixture of 1 mole of dihydrogen phosphate and 1 mole of hydrogen phosphate.
81	3	Carbon and oxygen, carbon monoxide, carbon dioxide.
82	4	Weigh, treat with hydrochloric acid, rinse, dry, and weigh again.
87	6	Burn, dissolve the oxide in alkali solution, and precipitate with an acid.
87	7	Dissolve in alkali solution, precipitate with an acid, rinse the precipitate, dry, and calcine.
124	7	Calcium carbonate.
125	11	Calcium, oxygen, carbon.
125	12	First goes down, and then lights up again.
143	5	Steel.
143	6	The first nail had been heated above the point at which iron modifications convert into one another and then cooled slowly; the second nail had been hardened; the third nail had been annealed after hardening.

Mendeleev's Periodic

Periods	Series	GROUP OF				
		I	II	III	IV	V
I	1	1 H Hydrogen 1.00797				
II	2	3 Li Lithium 6.939	4 Be Beryllium 9.012	5 B Boron 10.811	6 C Carbon 12.01115	7 N Nitrogen 14.007
III	3	11 Na Sodium 22.990	12 Mg Magnesium 24.312	13 Al Aluminium 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974
IV	4	19 K Potassium 39.102	20 Ca Calcium 40.08	Sc 21 Scandium 44.956	Ti 22 Titanium 47.90	V 23 Vanadium 50.942
	5	Cu 29 Copper 63.546	Zn 30 Zinc 65.37	31 Ga Gallium 69.72	32 Ge Germanium 72.59	33 As Arsenic 74.922
V	6	37 Rb Rubidium 85.47	38 Sr Strontium 87.62	Y 39 Yttrium 88.905	Zr 40 Zirconium 91.22	Nb 41 Niobium 92.906
	7	Ag 47 Silver 107.868	Cd 48 Cadmium 112.40	49 In Indium 114.82	50 Sn Tin 118.69	51 Sb Antimony 121.75
VI	8	55 Cs Cesium 132.905	56 Ba Barium 137.34	La * 57 Lanthanum 138.91	Hf 72 Hafnium 178.49	Ta 73 Tantalum 180.948
	9	Au 79 Gold 196.967	Hg 80 Mercury 200.59	81 Tl Thallium 204.37	82 Pb Lead 207.19	83 Bi Bismuth 208.980
VII	10	87 Fr Francium [223]	88 Ra Radium [226]	Ac ** 89 Actinium [227]	Ku 104 Kurchatovium [264]	
Higher oxides		R_2O	RO	R_2O_3	RO_2	R_2O_5
Hydrogen volatile compounds					RH_4	RH_3

* Lanthanides	Ce 58 Cerium 140.12	Pr 59 Praseodymium 140.907	Nd 60 Neodymium 144.24	Pm 61 Promethium [145]	Sm 62 Samarium 150.35	Eu 63 Europium 151.96
** Actinides	Th 90 Thorium 232.038	Pa 91 Protactinium [231]	U 92 Uranium 238.03	Np 93 Neptunium [237]	Pu 94 Plutonium [242]	Am 95 Americium [243]

Table of the Elements

ELEMENTS					
VI	VII	VIII			
	(H)				2 He Helium 4.003
8 O Oxygen 15.9994	9 F Fluorine 18.998				10 Ne Neon 20.183
16 S Sulphur 32.064	17 Cl Chlorine 35.453				18 Ar Argon 39.948
Cr 24 Chromium 51.996	Mn 25 Manganese 54.938	Fe 26 Iron 55.847	Co 27 Cobalt 58.933	Ni 28 Nickel 58.71	
34 Se Selenium 78.96	35 Br Bromine 79.904				36 Kr Krypton 83.80
Mo 42 Molybdenum 95.94	Tc 43 Technetium [99]	Ru 44 Ruthenium 101.07	Rh 45 Rhodium 102.905	Pd 46 Palladium 106.4	
52 Te Tellurium 127.60	53 I Iodine 126.904				54 Xe Xenon 131.30
W 74 Tungsten 183.85	Re 75 Rhenium 186.2	Os 76 Osmium 190.2	Ir 77 Iridium 192.2	Pt 78 Platinum 195.09	
84 Po Polonium [210]	85 At Astatine [210]				86 Rn Radon [222]
RO_3	R_2O_7	RO_4			
RH_2	RH				

Gd 64 Gadolinium 157.25	Tb 65 Terbium 158.924	Dy 66 Dysprosium 162.50	Ho 67 Holmium 164.930	Er 68 Erbium 167.26	Tm 69 Thulium 168.934	Yb 70 Ytterbium 173.04	Lu 71 Lutetium 174.97
Cm 96 Curium [247]	Bk 97 Berkelium [247]	Cf 98 Californium [249]	Es 99 Einsteinium [254]	Fm 100 Fermium [253]	Md 101 Mendelevium [256]	(No)102 (Nobelium) [255]	(Lr) 103 (Lawrencium) [257]

Solubility

ions	H^+	NH_4^+	K^+	Na^+	Ag^+	Ba^{2+}
OH^-		S	S	S	—	S
NO_3^-	S	S	S	S	S	S
Cl^-	S	S	S	S	I	S
S^{2-}	S	S	S	S	I	S
SO_3^{2-}	S	S	S	S	P	P
SO_4^{2-}	S	S	S	S	P	I
CO_3^{2-}	S	S	S	S	P	I
SiO_3^{2-}	I	—	S	S	I	I
PO_4^{3-}	S	—	S	S	I	I
CH_3COO^-	S	S	S	S	S	S

S — soluble
(more than 1 g in 100 g of water)

P — poorly soluble
(from 0.001 g to 1 g in 100 g of water)

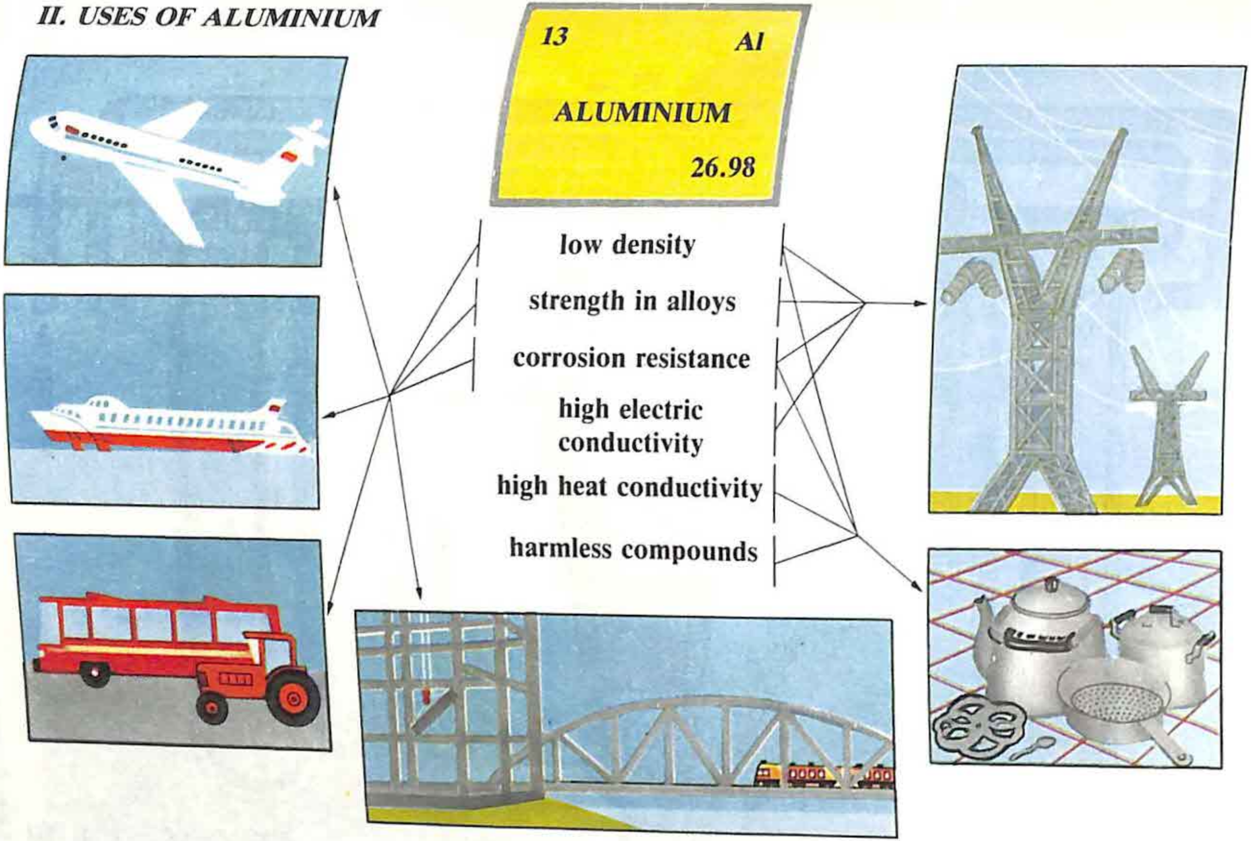
Table

Ca^{2+}	Mg^{2+}	Zn^{2+}	Cu^{2+}	Hg^{2+}	Pb^{2+}	Fe^{2+}	Fe^{3+}	Al^{3+}
P	P	│	│	—	P	│	│	│
S	S	S	S	S	S	S	S	S
S	S	S	S	S	P	S	S	S
—	—	│	│	│	│	│	│	—
P	S	P	—	—	│	P	—	—
P	S	S	S	—	P	S	S	S
│	P	P	—	│	│	│	—	—
│	│	│	—	—	│	│	—	—
│	P	│	│	│	│	│	│	│
S	S	S	S	S	S	S	S	S

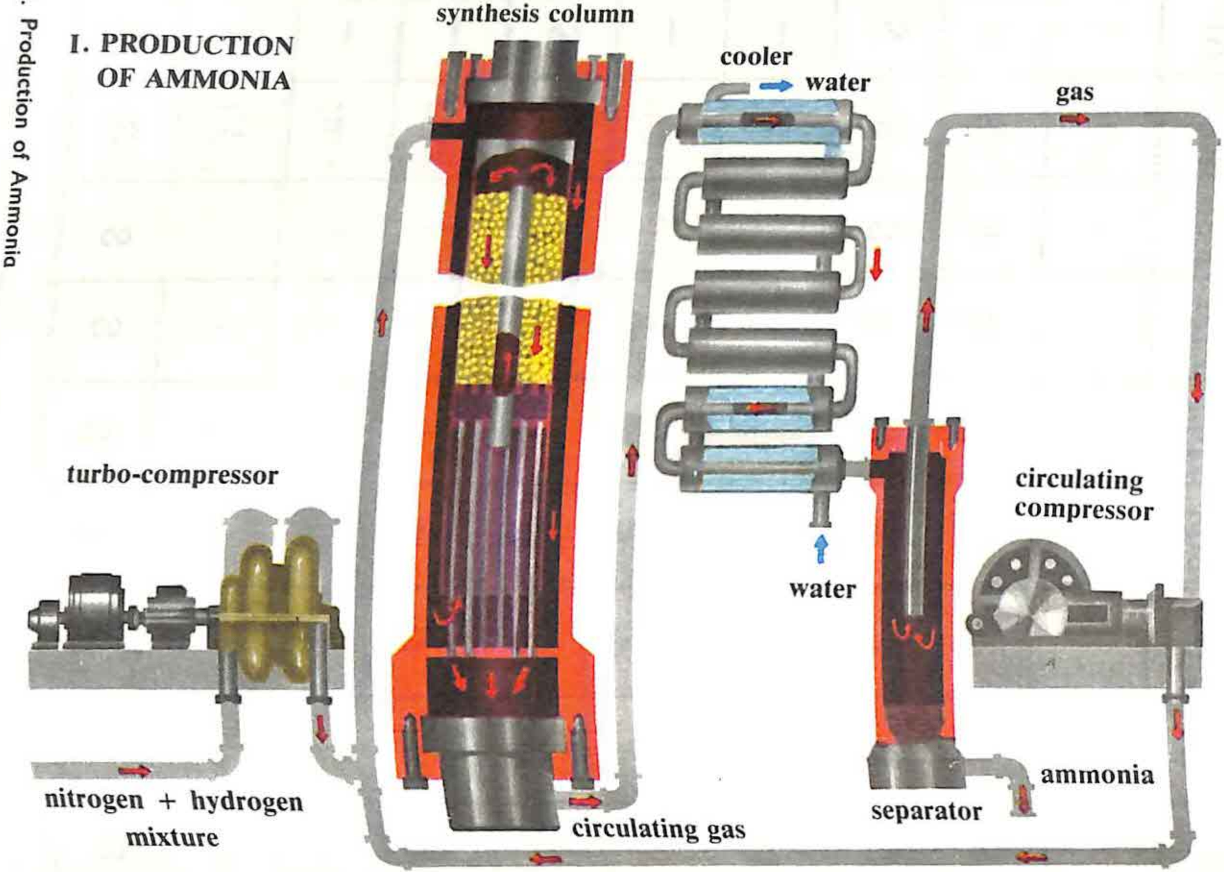
│ — insoluble
(less than 0.001 g in 100 g of water)

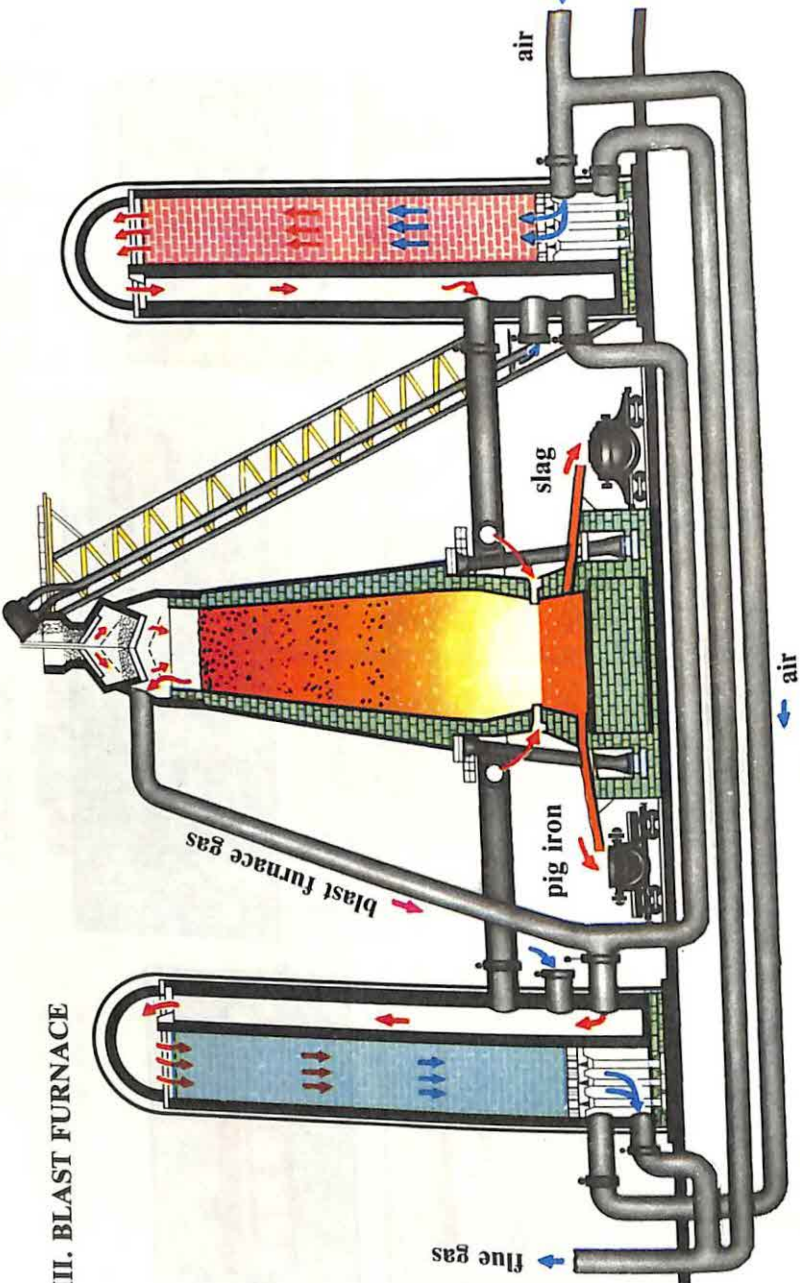
— — decomposed by water or do not exist

II. USES OF ALUMINIUM



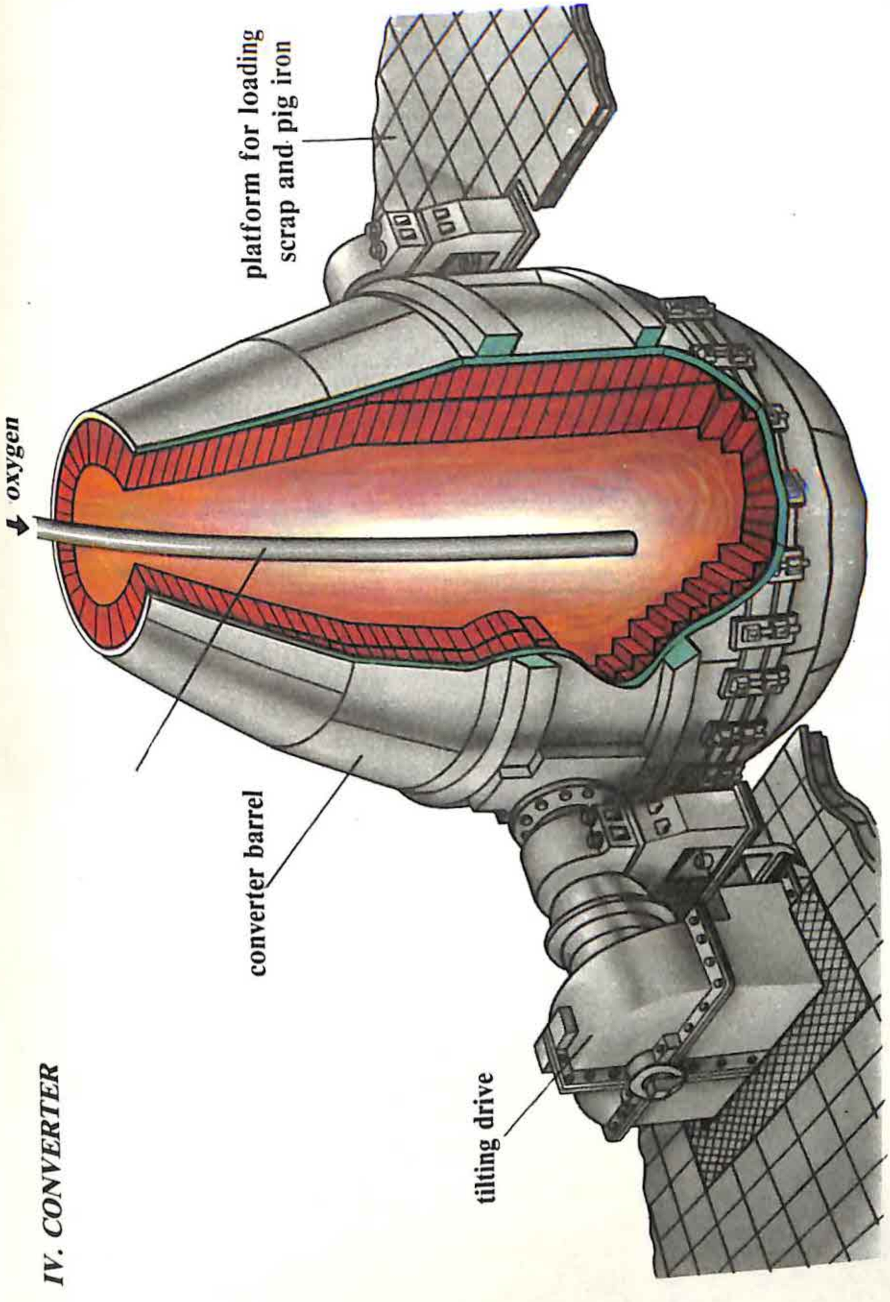
I. PRODUCTION OF AMMONIA





III. Blast Furnace

IV. CONVERTER



IV. Converter

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Other Mir Titles

Elementary Order (Mendeleev and his Periodic System)

I. PETRYANOV, Mem. USSR Acad. Sc.
and
D. TRIFONOV, D. Sc. (Chem.)

The periodic system of chemical elements has been compared to the multiplication table in view of the essential part it plays in modern chemistry and not only chemistry but many other sciences. But while the multiplication table must be simply learned by heart, the periodic system of elements should be first of all understood. One must analyze its structure and understand its regularities and then one can use it as a veritable encyclopaedia of chemical knowledge.

The book has been written specially for teenagers by a well known historian of chemistry and a prominent physical chemist.

Contents. How the Great Law Was Discovered. Difficult Path of the Periodic Law. The Periodic Law Determines the Atomic Structure. Artificial Elements. A Look into the Future. The Ever-Present Law.

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Notions
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A.I. BUSEV and I.P. EFIMOV

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